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# INORGANIC CHEMISTRY

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BY HORACE G. BYERS

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Chemistry, Inorganic - Textbooks,  
1917

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Byers





**INORGANIC CHEMISTRY**

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# INORGANIC CHEMISTRY

BY

HORACE G. BYERS

PROFESSOR OF CHEMISTRY IN UNIVERSITY OF WASHINGTON

ILLUSTRATED

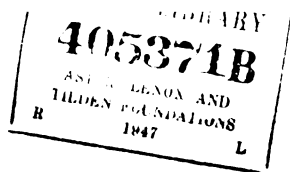
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## PREFACE

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FOR eighteen years the author has found himself confronted by large elementary classes in chemistry. Some students have had high school preparation in chemistry while others have not. Though the types of students are kept in separate classes the ground covered must be essentially the same. In both groups there are many students beginning the study as a life task. More of them desire chemistry as a tool to be used in the various professions in which they hope to engage; others wish to have the course as a complement to a liberal education; still others, alas, do not wish it at all but have to take it. The course outlined in the following pages is the result of an effort to provide something of value to all these students. The time required adequately to cover the ground is a three-hour lecture course for one year, for students with high-school chemistry, and a year and a half for those not so prepared. How well the task has been done only others may say.

The following points should be kept in mind: the text should present accurate and extensive information; it should present this information in strictly scientific form; observation of facts and classification should precede generalization; the need for hypotheses should be felt before they are offered, and when presented their purposes and limitations should be clearly shown; the theories of science should be presented as such and not as established truths, and should be justified only so far as the facts permit and their utility warrants, and this method should be consistently used. The desire for accurate and precise information should not lead the instructor to ignore the general continuity of natural phenomena; the course should widen in scope and, in a sense, increase in difficulty as the subject is developed. With a mixed body of students the text should demand a minimum degree of application to study on the part of all students and should provide an outlet for the activities of the most industrious; the course should provide a survey of the whole field of chemistry and in such form that as little as may be will have to be "unlearned" in subsequent courses; finally, the course should be *human* and show sufficient points of contact with the other activities of the student as to make evident that chemistry

is a vital factor in the life of every one and a portion of the much wider field of science.

Whether the text meets these needs in a satisfactory manner is more than doubtful, but at least the attempt to accomplish this end has been made. The subject matter has been carefully arranged and forward references are frequently given, not only for the sake of zealous students but also to show the need for things not yet presented. Back references are also given both for emphasis and review, and also to promote the recognition of the relationship of topics. Citations of books, magazines, and journals are made not only for their own sake but to widen the horizon of the student. So far as possible, the historical order of presentation is followed and some special emphasis placed on this phase of the subject. The hypothetical phases have been segregated and expressed as such and as clearly as possible. The laws are stated as simply as possible while yet keeping them free from dogmatic assertion. So far as limitations of space permit the connection between chemical topics and human activities of other sorts is pointed out. Special care has been taken to emphasize the relationship between chemical energy and the other forms of energy. In attempting these things it is hoped that the development of the subject is sufficiently gradual that no fairly industrious student with average ability need be led into a "Slough of Despond."

The material contained in the text has been secured from any available source and no claim is made for any special ownership in it. Were it possible to do so it would be a pleasure to credit every source. The experienced reader will undoubtedly note the influence of Alexander Smith upon the general character of the text. This is due not only to admiration for the teaching method of Dr. Smith, but also to the fact that the General Inorganic Chemistry has been used by the author as a text for many years. Mellor's Modern Inorganic Chemistry has also proved a "very present help in trouble." The author, however, believes himself free from plagiarism and yet freely acknowledges his indebtedness to others. He also owes a debt of gratitude to his wife, Dr. H. L. Trumbull, Dr. R. E. Rose, and Dr. F. H. Heath for helpful criticism and proof reading and to Mr. W. R. Gailey for the drawings from which the cuts are made.

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# INORGANIC CHEMISTRY

## CHAPTER I

### INTRODUCTION

*Science and the Relation between the Sciences.*—In the process of gaining knowledge the student is confronted by an enormous number and variety of phenomena. If this mass of material is to be rendered useful it must be sorted and arranged in some manner so that the knowledge one possesses may be available at the proper time and for the purpose in hand. It is the function of Science to supply this need. **Science** may be defined as knowledge, gained by observation, experiment and reasoning, coordinated, arranged and systematized according to definite plans. It may concern itself with any subject. A collection of facts does not represent science unless such collection is systematized. The mass of such systematized knowledge is so great that it is customary to subdivide it into a number of parts each of which is called a **Science**. This subdivision of science is only for convenience and it has been found impossible to separate it into wholly independent parts. It is important to know and to remember that no one can gain control of any one science without considerable knowledge of several other sciences. There are two general types of sciences, abstract and concrete. The abstract sciences deal mainly with forms of abstract reasoning. Concrete sciences deal mainly with matter and the changes which it undergoes and may undergo. This division is wholly arbitrary and does not exist in the subjects themselves. Thus mathematics, which is essentially abstract in that it deals with principles which exist without reference to any particular object, nevertheless also deals with real matter and its applications are frequently concrete. On the other hand, physiology which is essentially concrete in that it deals with the structure and functions of plants and animals also deals with principles and ideas which are not dependent upon any particular body. We

find also certain sciences in which the abstract and concrete features are so mingled as to render even this rough division difficult. An example of such a science is psychology.

The great body of knowledge, **Natural Science**, is for convenience of study frequently divided into the following groups of sciences:

Physical sciences.	Biological sciences.	Psychological sciences.
Physics Chemistry Geology Astronomy .....	Botany Zoology Bacteriology ..... .....	Psychology Sociology Economics History Language

Each member of these groups embraces, as its chief concern, the facts connected with one phase of nature but not these exclusively. The subjects merge into one another and are to a degree coextensive. For example, zoology, which concerns itself chiefly with animals, also includes topics which belong to the sciences of botany, chemistry, physics, and geology. It is impossible therefore to define accurately the boundaries of any one science. It is perhaps unfortunate, from the standpoint of convenience of study, that we cannot subdivide nature into small mutually-exclusive sections, the facts concerning which might be tabulated and pigeonholed in a perfectly orderly manner. Nature is not discontinuous and each phase merges imperceptibly into some other phase or phases. It is certainly unfortunate in view of this fact that scientific study of the several **branches** is so exclusively pursued that the student is likely to forget, or even never learn, that there is a parent stem, nature in general, which deserves attention. One of the above branches of science is **chemistry**. This science deals, in the main, with the properties and composition of matter and with changes produced by various agencies under diverse conditions. Thus a knowledge of the chemistry of sugar would include such points as its color, taste, and specific weight, whether it is a simple or complex substance, what will happen to it when heated, alone or with other substances, and many like topics. A knowledge of the chemistry of water would include the properties by means of which it may be described, whether it is a simple or a complex substance, what happens when it comes in contact with other substances, what effects are produced upon it by heat, etc. The subject is vast and, like science in general, may be subdivided when any



advantage is gained by so doing. We have as examples of commonly recognized subdivisions, General Chemistry, Organic Chemistry, Physiological Chemistry, Analytical Chemistry, Physical Chemistry, etc. Each of these has its special province, though not independent, and for convenience each may be studied or developed as a separate subject. **General Chemistry**, which is the special topic of the present discussion, is itself frequently divided into descriptive and experimental chemistry. We shall endeavor so to combine both as to furnish a comprehensive view of chemistry, what it is, what principles are followed in the classification of its facts, how the facts were learned, and also what hypotheses have served in the development of the subject. In addition we shall attempt to show its relation to daily life and its points of contact with other subjects.

**Elements.** — **Matter** is a term used to describe anything which occupies space and possesses the property of weight. As we encounter it there seem to be an infinite, or at least a very indefinitely large number of sorts. In our study of the composition of matter it is our first business to see whether any simple method can be arrived at by means of which the great variety of kinds of matter can be brought into simple relations with each other. This can be done if we can but find a limited number of simple forms of matter out of which the others are made. In the past many efforts have been made to accomplish this. One of the most famous of these was made by the early Greeks and found expression through Aristotle. He supposed all matter to be made up of varying degrees of the properties of moistness, dryness, heat and cold. These properties found fullest expression in water, earth, fire and air and hence these are called the Aristotelian elements and the use of the words in the sense of elements finds frequent expression in literature even at present. Another effort of the same kind was made by the alchemists. The alchemists were men who, during the Middle Ages, sought information concerning matter mainly for the purpose of learning how to make gold from less valuable metals. They supposed all the varieties of matter to be made of different proportions of salt, sulfur and mercury. It is probable that they meant by these terms not the substances themselves but rather the peculiar properties represented by them. In any event neither of these suppositions has proved a satisfactory basis upon which to classify the various forms of matter.



When the problem was attacked **experimentally** a different solution of it was reached. The method may be illustrated as follows: Suppose we have before us three quite different substances, charcoal, water and sugar. By heating the sugar we are able to separate it into water and charcoal, and therefore so far as this experiment is concerned it seems that sugar is composed of two simpler forms of matter. Again, it is possible to show experimentally, though the operation is somewhat more complex, that the substances, iron, sulfur, iron pyrites and iron sulfide present but two **simple** forms of matter, iron and sulfur, and that the pyrites and sulfide yield iron and sulfur when separated. Also it is possible to show that the common substances alcohol, ether, formaldehyde, sugar and many others can be divided so as to produce carbon, hydrogen and oxygen and that no other things enter into their composition. It may be shown, however, by further investigation that these simpler forms have never been broken down or in any way shown to be made up of other forms of matter. In this manner scientists have shown that all the multitude of known substances, so far investigated, are either simple forms of matter or are made up of a limited number of simple forms. **The forms of matter not yet shown to be complex are called elements** and the total number known at present is about ninety. The list is given on the inside back cover of this volume. It is to be understood that the list is incomplete. Some forms which we now consider simple may be shown to be complex and the constituents may be new elements or ones already known and so the list may be increased or diminished. It is also probable that new elements remain to be discovered. It is not to be supposed that this view of the elementary composition of matter was the product of one mind or that any one person developed the complete list of the elements. Both are a product of growth through centuries from the time of Robert Boyle (1678) to the present. It is to Lavoisier (1789) that we owe the clear statement that an element is a substance not yet shown to be complex. This view has been the guide which has led to the development of our present list. (More modern views are modifications of that of Lavoisier, cf. Chapter XXXVI.)

The elements may be considered as the component parts of all known substances in much the same manner as the letters of the alphabet are the component parts of words. When we remember that twenty-six letters in different combinations give rise to the multitude of words in the dictionary we need not be surprised at

the number of different substances. The study of chemistry is no more hopeless because of the multitude of substances than is language because of the multitude of words.

The elements are not all of like importance. Some are rare and of small practical value. Others are rare but, because of some special use to which they, or substances of which they are a part, are put, are of exceeding interest. Still others are abundant but of relatively little interest because of small practical application.

The amounts of eighteen of the elements found in those portions of the earth which we are able to examine are given in the following table. (The estimates are those of F. W. Clarke.)

	Per cent		Per cent		Per cent
Oxygen.....	49.85	Potassium.....	2.33	Phosphorus.....	0.10
Silicon.....	26.03	Magnesium.....	2.11	Fluorine.....	0.10
Aluminium.....	7.28	Hydrogen.....	0.97	Sulfur.....	0.10
Iron.....	4.12	Titanium.....	0.41	Barium.....	0.09
Calcium.....	3.18	Chlorine.....	0.20	Manganese.....	0.08
Sodium.....	2.33	Carbon.....	0.19	Nitrogen.....	0.03
					99.51

It is to be observed that all the remaining elements together amount to less than half a per cent and a comparison with the full list will show that these include such familiar substances as copper, lead, tin, etc.

**Types of Change.**—The student of chemistry is not only confronted by a huge variety of different substances but also by an apparently bewildering number of changes. No object in nature remains permanently fixed. Changes of position, of temperature, of electrical condition, of composition, etc., are constantly taking place. There are, however, two distinct types of change. One of these types may be illustrated by the changes taking place when a platinum wire is heated in a gas flame. We may observe that the wire changes color, it becomes a source of light, it becomes slightly longer and thicker and when the exciting cause of these changes, the gas flame, is removed the wire speedily regains its normal size and appearance. Another example of the same type of change is furnished by passing an electric current through a coil of wire which surrounds a rod of soft iron. Previous to the passage of the current and after its discontinuance the iron seems wholly



inert with respect to iron filings placed near it. During the passage of the current the iron core possesses a strange attraction for the filings and they cling to it with remarkable pertinacity. Such changes as these might be instanced in great numbers and in all we should find that the body undergoing the change may at all times be recognized as the original material, *i.e.*, it does not lose its identity. More than all else these changes are always to be recognized as gradual. For example, the heating of the wire was gradual even though very rapid. Between the complete establishment of the maximum attractive power of the magnet and the absence of the same there was a period of partial magnetization. Even in the most adroit movements of the prestidigitator we are perfectly sure of the existence of the object of his manipulations somewhere between its appearance in one place and its subsequent appearance in another. Such changes as these are called **physical changes**, and are specially distinguished by the facts mentioned. **The objects changed do not lose their identity and the changes are gradual.** We encounter other changes which may be sharply contrasted with such as are above described. If we heat a magnesium wire in a gas flame we have an evolution of light and expansion in volume, yet the most careless observer cannot but note the change in the appearance of the wire. It was a lustrous metal, it has become a soft white powder and moreover there appears to be no intervening condition between that of coherent metal and of white powder. Another example of this sort of change is furnished by passing an electric current through a solution of copper sulfate. It will be noted that one of the electrodes becomes coated with copper and that bubbles appear at the other. If the electrodes are of platinum and the operation be continued sufficiently long the solution becomes colorless. Such changes are typical **chemical changes** and are marked specially by the loss of identity of the material changed and by the abruptness of the change. (The student should note that the terms 'abrupt' and 'gradual' as used above do not refer to time.)

It is with this last type of change that the chemist has more particularly to do and familiar examples of such changes might be cited in large numbers. We should note, however, that while this division of changes into two general types is helpful, we shall in some instances find it difficult to distinguish whether a given change is physical or chemical. We must recognize this inherent difficulty in all classifications of natural phenomena.

**Definition of Terms.** — Each special subject has a language of its own and the student of the subject must learn to speak that language. The chemist uses many ordinary terms in special senses or in one of the varied senses in which a given term may be popularly employed. It is therefore desirable before proceeding with further study of the features common to all chemical changes to define a few of these terms.

A **body** of matter is to the chemist any portion of matter which he has under consideration. It may be simple or complex, but the term always refers to some definite concrete thing. A **substance**, on the other hand, refers to some particular kind of matter. It may be simple or complex, but in speaking of a substance we do not refer to any particular body. Thus we may say that a given body of matter, *e.g.*, a chair, is made of a substance, wood, or a given piece of money may be a piece or body of gold, but gold is, in general, a substance.

By the term **properties**, as applied to bodies, we understand the different means by which these bodies become evident to our senses. The properties of a body may belong to it merely because of its separate existence as a body, *e.g.*, size, weight, shape, or they may belong to it as a temporary condition due to environment, *e.g.*, temperature, electrical condition. Still other properties of a body are attributes of (*i.e.*, are inseparable from) the substance or substances of which a given body is composed. The properties of a substance which are used as a means of identification we call **characteristic properties**. We recognize two general types of properties of substances, **physical properties** and **chemical properties**. The former are those possessed by a substance in a given condition, or are called into existence by some physical change which a body of that substance may undergo. The latter are manifested only when a substance undergoes a chemical change. An illustrative example will probably make the use of these terms clear. If we examine a **body** of sulfur we find that the shape, size and temperature do not depend upon the **substance** since any other substance may possess the same properties. The color, solubility and density of sulfur are **physical properties**, though each may be somewhat altered as a given body undergoes physical changes. Of the physical properties the color, taste, density, melting point, and solubility may be called characteristic since by observing a sufficient number of these we may establish the identity of the body as being a portion of the substance sulfur. If we heat



the sulfur in the flame of a Bunsen burner it will burn and give rise to a disagreeable odor. This is a chemical property and is also characteristic because the odor is only developed by chemical change and its formation assists in establishing the identity of a given body as being sulfur.

The word **fact** is in ordinary language used to express a real state of things as distinguished from a statement of belief. In science the word usually denotes anything which is established directly by experiment as distinguished from that arrived at through theory.

In the preceding discussion of chemical change attention was called to the fact of loss of identity when magnesium is burned. Again the fact of loss of identity is shown when copper sulfate is decomposed by the electric current. When a sufficient number of such facts have been accumulated to convince us that when any chemical change takes place the materials changed lose their identity we may express this observed uniform mode of behavior in a single statement. Such a statement is called a **law of nature** or a **generalization**. A **natural law** is a statement of an observed uniform mode of behavior of nature. Such laws are markedly different from mandatory laws imposed by some superior authority such as church or state. A law of nature may not be 'disobeyed' since no command exists. When a supposed natural law is found not to accurately describe the uniform mode of behavior it purports to describe, it ceases to be a law.\*

**Kinds of Chemical Change.**—1. **Decomposition.** If we heat some saltpeter in a hard glass test tube over a Bunsen burner the mass first melts and so far as can be seen no other change takes place. (A physical change.) If the melted mass be still more strongly heated it appears to boil but, unlike in boiling water,

\* Of course where a law describes a mode of behavior of a class of substances and instances become known where such a description is inaccurate we may at our option change the basis of classification so as to exclude these instances or we may discard the law. Where the proper classification is in doubt the generalization becomes doubtful. Thus in the above case if we should observe a change which is not accompanied by loss of identity but which for other reasons we should like to class as chemical we may follow one of three courses. We may say that the law should not exist, we may say the change under discussion is an exception, or we may class the change as physical and not chemical. Which of these courses is followed is determined by convenience or by convention.

there is no fog produced at the mouth of the tube. If now we introduce a splinter on the end of which is a spark, the spark, instead of going out as it would do in air, bursts into flame. If the heating be long continued the material which causes the spark to flame ceases to form and on cooling we find a residue which is not the same as the original material. That this is true may be shown by treating a small quantity of each in a test tube with some dilute sulfuric acid. The two behave quite differently. This experiment illustrates one sort of chemical change. The saltpeter has been decomposed by heat. We shall meet many cases of the same sort in which by means of heat, or some other agency, a substance is broken up, giving rise to others. Such a change is called **decomposition**.

2. **Synthesis.** If sulfur and powdered iron are thoroughly mixed on a piece of paper, a grayish mass is obtained which certainly does not look like either original substance, but the presence of both as separate substances may be shown by means of a magnet. (A physical change.) If the mixture is heated in the burner, we find that shortly a dull red glow appears in the tube and, even if removed from the flame, the glow spreads through the whole mass. When cooled and examined this material no longer exhibits the appearance of iron and sulfur, even if examined with a magnifying glass. Nor, if sufficient sulfur were used, does a magnet attract it either as a whole or partially. By sufficiently drastic treatment it may be shown that this mass may be made to yield both iron and sulfur. These substances have therefore been combined to form a third. The new substance is known as iron sulfide. Such changes as this are very numerous, also, and are known as **combinations**, or **syntheses**.

3. **Exchange.** If copper sulfate is dissolved in water and to the solution is added some sodium hydroxide, a bluish white substance separates from the liquid which is clearly not either of the original substances, since if we remove the liquid by pouring through a filter paper, the portion which remains on the paper does not behave as either of the original substances when heated. If the exactly proper amount of sodium hydroxide is used, we may, by heating the liquid portion (the filtrate), obtain still another substance which is wholly different from either original material. Extended investigation shows that these two new substances each contain a **part** of each of the original ones. The full significance of the **names** will not be apparent to the beginner but the idea now



sought will be clear when we say that the copper sulfate and sodium hydroxide when brought together form copper hydroxide and sodium sulfate. This is a case of **exchange** and furnishes a third variety of chemical change. It is also known as **double decomposition** and as **metathesis**.

These three kinds of chemical change, **decomposition**, **combination**, and **exchange**, embrace all chemical changes which exist, with the exception of one variety which will be more fully discussed later and is known as **intramolecular rearrangement**. (See p. 339.) If the statement just made is true, then it is apparent that in all chemical changes there is a change in composition, either by addition, division, exchange, or rearrangement of parts. This then may be considered a characteristic of chemical change.

**Importance of Physical Properties.** — It is worth noting at this point that if all the experiments previously described are carried out we do not see any chemical change, nor are any chemical properties visible. Thus, when iron and sulfur are heated, we see an evolution of light, we feel an increase in temperature, and we note a change of physical properties from the extent and character of which we infer that a chemical change has taken place. In such operations it is therefore important to distinguish between physical properties which are to the purpose in hand. We shall therefore present in some detail a few of the phenomena which always accompany chemical actions. The student will gradually acquire the art of picking out properties which serve as indications of chemical change and those which have but little or no bearing on chemical questions. The art of selective attention is one which must be acquired in any special study before rapid progress is made.

**The Law of Conservation of Mass.** — In many instances superficial observation of the results of chemical change might lead to the conclusion that matter is destroyed. For example, a lump of coal when placed on the fire gradually disappears leaving only a small amount of ash. Again a lighted candle made of tallow or wax will practically completely disappear from sight. Similar instances of changes ordinarily classed as physical changes may also be cited. Thus water, camphor and many other substances, if placed in open vessels, gradually disappear. If we warm a quantity of brandy or whiskey it loses its intoxicating properties



and, as the alchemists said, its **spirit** is removed. In all these instances there is a loss of weight of the material undergoing the change and, in the absence of evidence to the contrary it might be assumed that matter is being destroyed. In all such cases, however, by using proper methods it may be shown that the matter does not absolutely disappear, but simply changes its form. In all the cases mentioned above the new forms happen to be invisible. In the case of the candle this may be shown by burning it in a chimney, and by means of a filter pump, drawing the products over soda

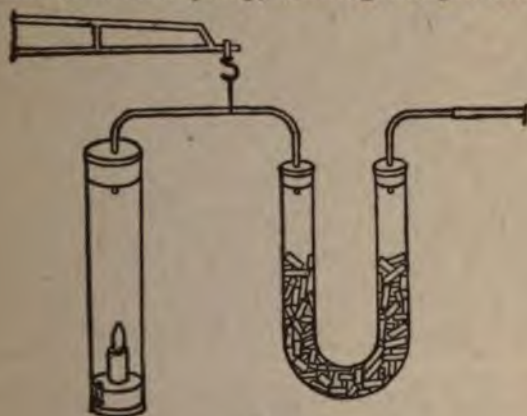


FIG. 1.

lime. The apparatus is sketched in Fig. 1. If the soda lime is weighed before and after the process it will be found to have increased in weight. Indeed if the candle and soda lime are both weighed it is found that far from the burning producing a loss of weight, there is actually an increase in total weight. It would seem to appear then that chemical changes may produce matter. Many instances of such apparent increase of matter by change might be cited, but one will suffice for our purpose. If we weigh a quantity of steel wool and burn it and weigh again, taking care to collect all the particles of material, we will note a very marked increase in weight. Since we found in the case of the burning candle that the apparent destruction of matter was not real, the question now arises, is the increase in weight due to production of matter? A convenient method of determining the source of the increase of weight in the case of the steel wool is to moisten some of it and insert it in a cylinder which is full of air. This cylinder is

set mouth down in a vessel of water. A substance very similar to that produced by burning the wool is slowly formed and a decrease in the volume of air in the cylinder will be noted. Lavoisier, a French chemist, in 1774, showed that in a number of



FIG. 2.

such cases the gain in weight is exactly equal to the weight of air absorbed. The final conclusion from a great number of similar determinations is that in no change, whether physical or chemical, has there been observed either gain or loss of weight if we take into account all the substances involved in the change. This is known as the law of conservation of mass. A very satisfactory illustrative experiment is as follows: Fill one limb of a  $\Lambda$  tube with potassium chromate and the other with silver nitrate solution. Seal the open end (see Fig. 2) and weigh. Mix the contents of the tube and again weigh. A very striking chemical change has taken place but no change in weight has occurred. So far as has been definitely determined the same result is always obtained when the egress or ingress of material is accounted for. Hence the law (*cf.* Mendelejeff, vol. 1, pp. 5-20).

**The Law of Definite Proportions.**—If some finely divided pure copper is heated in a current of air until it is completely converted into a black substance known as copper oxide, it is found on comparing the weight of the oxide and of the original copper that the ratio is, approximately, 1 : 0.7996. The more frequently and the more carefully the experiment is performed the more closely the results obtained approach the ratio given. That is, copper oxide is 79.96 per cent copper; the rest of the substance is oxygen. Experience has shown that so long as the product is wholly the black oxide, the percentage of copper is never more or less than 79.96 to an extent beyond the known limits of error of measurement. Again, if a weighed quantity of iron is heated with sulfur, the resulting compound exhibits the weight ratio, iron sulfide : iron :: 1 : 0.6352 as the mean of a series of very accurate determinations, *i.e.*, the sulfide is 63.52 per cent iron and 36.48 per cent sulfur. This result is obtained no matter how large an amount of sulfur is used since any excess is volatilized by heating. If too little is used, the resulting mass may be shown to contain unchanged iron. These cases illustrate the determination of the composition



of substances by **synthesis** (*συντίθεν* = to put together), i.e., by putting known quantities of the constituent parts together to form the new substance. The same result might be reached in both cases by another method. If we take pure black copper oxide and remove the oxygen by passing hydrogen (for details see composition of water) over it, the resulting copper will be found to bear to the original oxide the same ratio as before. Or if iron sulfide is subjected to a more complicated process which need not be here described, the composition is found to be as before stated. This method of determination is known as **analysis** (*ἀναλύειν* = to loosen). In the first decade of the nineteenth century, Proust demonstrated, what had been tacitly assumed by many others, that many substances when their composition is determined by either of the above methods give similar results. Such substances we call **compounds** and the rule may be stated: **A pure compound always contains the same elements in constant ratio by weight.** This statement is known as the **law of definite proportions**. By a multitude of researches it has been shown to be rigidly true for many substances. In those cases where bodies of matter are found in which a constant ratio of the constituents does not obtain it is frequently apparent that no chemical change, at least as judged by the criterion given on page 16, has taken place at all. In such cases we call the bodies **mixtures**. For example, we may have two or more substances such as iron and sulfur, or sand and sugar, existing side by side in any desired ratio by weight. Mixtures are distinguished ordinarily by a lack of homogeneity and frequently may, by some purely mechanical means, be separated, partially at least. There are, however, still other cases of substances which have an inconstant ratio of constituents and yet are homogeneous. Their formation may be accompanied by loss of identity of the constituent materials and by other characteristics of chemical change. Examples of such changes are furnished by the solution of sugar and of many other substances in water, and by the formation of alloys, such as gold, silver or bronze coins, all of which are composed of more than one element. The nature of the relation between the constituents in such cases is not yet wholly clear to chemists. We call such combinations **solutions**. We use therefore, practically, the following classification of matter. (1) **Elements:** substances not yet shown to be complex. (2) **Compounds:** substances composed of more than one element and in which the law of definite proportions obtains. (3) **Mixtures:** combinations

of two or more substances the formation of which is accompanied by no evidences of chemical change. (4) **Solutions:** an intermediate group of substances to which are assigned complex substances not clearly either pure compounds or mixtures (of this class much will appear in subsequent pages, *vide* Chapters IV and IX especially).

**The Law of Multiple Proportions.** — As a result of the study of the composition of compounds many instances are known in which two or more different substances consist of the same elements. The composition of three pairs of such substances is shown in the following table:

	Per cent	Per cent
Ethylene:	Carbon . . . 85.7	Hydrogen . . . 14.3
Marsh gas:	Carbon . . . 75.0	Hydrogen . . . 25.0
Carbon dioxide:	Carbon . . . 27.27	Oxygen . . . . 72.73
Carbon monoxide:	Carbon . . . 42.86	Oxygen . . . . 57.14
Nitrous oxide:	Nitrogen . . . 46.67	Oxygen . . . . 53.33
Nitric oxide:	Nitrogen . . . 30.43	Oxygen . . . . 69.57

In the first pair of substances it is clear at a glance that the quantity of hydrogen as compared with that of carbon is greater in marsh gas than in ethylene. How much greater it is, is shown by considering the quantity of carbon in both substances as unity. Then in ethylene  $85.7 : 14.3 = 1 : x$ ;  $x = 0.167$ . In marsh gas,  $75 : 25 = 1 : x'$ ;  $x' = 0.334$ . The ratio of  $x$  to  $x'$  is therefore  $1 : 2$ . A similar result is obtained if by the same method we compare the amount of oxygen in carbon dioxide with that in carbon monoxide, *e.g.*,

$$27.27 : 72.73 = 1 : x \quad \text{and} \quad 42.86 : 57.14 = 1 : x',$$

$$x = 2.66 \quad \text{and} \quad x' = 1.33 \quad \text{and} \quad \frac{x}{x'} = \frac{2}{1}.$$

The same sort of relation is also shown by the third pair of substances. If the analyses of the two common oxides of sulfur (*q.v.*) are examined in the same way, a similar result is obtained except that the ratio of the quantity of oxygen in one compound is to that in the other as  $2 : 3$ .

From a consideration of such results as those above given, and from certain theoretical considerations (presented in Chapter V) Dalton, in 1804, reached the conclusion that whenever more than one compound is formed from the same factors, if one of the fac-



tors is considered in a fixed amount, the amounts of the other in the different compounds will vary in simple ratio. This is known as the law of multiple proportions. The law has been abundantly verified by subsequent investigations. As examples we may cite the five oxides of nitrogen in which the amounts of oxygen in the different compounds which unite with a fixed amount of nitrogen are in the ratio of 1 : 2 : 3 : 4 : 5. We may also cite four oxygen acids of chlorine in which for a fixed amount of one factor, which is made up of chlorine and hydrogen, the oxygen varies in the ratio of 1 : 2 : 3 : 4. This remarkable generalization had a most important part in the development of the atomic hypothesis which is discussed in Chapter V.

**The Law of Combining Weights.**—When compounds are analyzed, we ordinarily express the results in the percentage of constituents. For example, if we have one gram of black copper oxide, we find it possible to obtain from it 0.7996 grams of copper and 0.2004 grams of oxygen. (See p. 12.) The composition, therefore, is copper 79.9 per cent and oxygen 20.1 per cent. We may prepare a list of such results and tabulate them as follows:

		Per cent		Per cent
Water:	Hydrogen . . .	11.19	Oxygen . . . .	88.81
Copper oxide:	Copper . . . . .	79.96	Oxygen . . . . .	20.04
Mercuric oxide:	Mercury . . . . .	92.59	Oxygen . . . . .	7.41
Ferrous oxide:	Iron . . . . .	77.8	Oxygen . . . . .	22.2
Litharge:	Lead . . . . .	92.82	Oxygen . . . . .	7.18

Although all the compounds contain oxygen, it does not appear at a glance how much, relatively, of each of the other elements is present. If, however, we should take for analysis instead of equal weights of each substance such quantities as would contain the same amount of oxygen, the relative weights of the other elements would be evident. These quantities may be calculated from the above data.

If we take the unit quantity of oxygen as eight, then we have in the case of water  $88.81 : 11.19 :: 8 : x$  and  $x = 1.008$ , i.e., 1.008 parts by weight of hydrogen are in combination with 8 parts by weight of oxygen in water. In a similar manner we may obtain for the above substances values as follows:

- Oxygen 8 : hydrogen 1.008, in water.
- Oxygen 8 : copper 31.8, in copper oxide.
- Oxygen 8 : mercury 100, in mercuric oxide.
- Oxygen 8 : iron 28, in ferrous oxide.
- Oxygen 8 : lead 103.45, in litharge.

1.008, 31.8, 100, 28, 103.45 are then the amounts of hydrogen, copper, mercury, iron, and lead which are equal in combining value to the same amount of oxygen.

It is of course possible to find in a similar manner the number of parts of any element which will combine with eight parts of oxygen. These relative amounts of the elements are known as **equivalent weights**. The five elements, other than oxygen, in the above list also combine with sulfur to form certain compounds called sulfides and with chlorine to form chlorides. When we express the composition of these compounds using the equivalent weights just ascertained a very surprising fact develops, as shown in the following table:

Hydrogen	1.008	: sulfur, 16.03, in hydrogen sulfide.
Copper	31.8	: sulfur, 16.03, in copper sulfide.
Mercury	100	: sulfur, 16.03, in mercuric sulfide.
Iron	28	: sulfur, 16.03, in iron sulfide.
Lead	103.45	: sulfur, 16.03, in lead sulfide.
<hr/>		
Hydrogen	1.008	: chlorine, 35.45, in hydrochloric acid.
Copper	31.8	: chlorine, 35.45, in copper chloride.
Mercury	100	: chlorine, 35.45, in mercuric chloride.
Iron	28	: chlorine, 35.45, in ferrous chloride.
Lead	103.45	: chlorine, 35.45, in lead chloride.

It appears that the same quantities of these five elements which are equivalent to a fixed amount of oxygen are also equivalent to fixed amounts of sulfur and of chlorine. What is found to be true in these instances has been found true for all elements. We may put the resulting generalization in the following form. *The relative amounts of the elements which combine with a fixed amount of oxygen are also equivalent when they combine with other elements.* This statement is known as the *law of equivalents* and also as the *law of reciprocal proportions*. If one considers the equivalent weights given above it is apparent that equal weight quantities of the elements are not of equal chemical value and it may be that these quantities of the elements may serve as convenient units for measuring the elements. This is indeed true. The above italicized statement must, however, be modified because of the fact that certain elements unite with each other in more than one ratio by weight. This we have already considered under the heading of the law of multiple proportions (p. 14). For example, in the case of copper and oxygen we have the two oxides in which



the ratios by weight are 8 : 31.8 and 8 : 63.6. In the case of iron and sulfur we have the weight ratio 28 : 16.03 in ferrous sulfide and 28 : 32.06 in iron pyrites. We have then as equivalent weights for copper both 31.8 and 63.6, and for sulfur 16.03 and 32.06. The relation existing between the different equivalent weights is expressible by small whole numbers. It is possible, therefore, to accurately express the composition of pure chemical compounds in terms of equivalent weights or multiples of the same by integers. It will be recalled that the unit of equivalent weights is oxygen with an arbitrarily selected value 8. Any other element might have been selected as a basis of comparison and any desired unit value assigned to it. For reasons which it is not desirable to present at present, but which are given in full in Chapter V, if we select 16 for a unit value for oxygen and certain of the corresponding equivalent values we secure a more convenient set of numbers by means of which to express the composition of compounds. These are known as **atomic weights**. The atomic weights are either the same as, or are small multiples of, the equivalent weights. The subjoined table gives a few of these and shows their relation to the equivalent weights. The full table appears on the inside cover of the text.

Element.	Equivalent weight.	Multiple.	Atomic weight.
Oxygen.....	8	2	16
Copper.....	31.8	2	63.6
Mercury.....	100	2	200
Lead.....	103.6	2	207.2
Iron.....	28	2	56
Hydrogen.....	1.008	1	1.008
Chlorine.....	35.45	1	35.45
Aluminium.....	9	3	27
Carbon.....	3	4	12
Sodium.....	23	1	23
Sulfur.....	16.03	2	32.06

If now we use these numbers to express the composition of some of the compounds already considered we find the following relations.

Water:	Oxygen....16,	Hydrogen.... $2 \times 1.008$ .
Cupric oxide:	Oxygen....16,	Copper.....63.6.
Cuprous oxide:	Oxygen....16,	Copper..... $2 \times 63.6$ .
Copper sulfide:	Sulfur....32.06,	Copper.....63.6.
Iron sulfide:	Sulfur....32.06,	Iron.....56.
Iron pyrites:	Sulfur.... $2 \times 32.06$ ,	Iron.....56.



This list may be extended indefinitely but we have sufficient illustrations to make the following statement clear. The composition of pure chemical compounds may be accurately expressed in terms of fixed numbers, called combining weights, or multiples of the same by integers, each element having its own combining weight. This statement is known as the law of combining weights. It is, perhaps, the most important single generalization in chemistry. The law of combining weights is not the result of one series of observations nor is it the result of the work of a single person. It has its beginning in the work of Richter (1792-1802) on the combining relations of the acids (Meyers' History of Chemistry, p. 190). It was advanced through the atomic hypothesis of Dalton, 1804, and the work of Berzelius (1808), but reached its present form only through the application of Avogadro's hypothesis (1811) by Cannizzaro (1860). Later a fuller presentation of how the atomic weights are obtained will be given. At this point the purpose is to make clear to the student that the elements are not measured in units of the same size, but each has, as it were, its own yardstick. The superior convenience of this means of expressing the composition of substances will not be apparent to the student at once, but will become increasingly evident as he proceeds with his work. He should be perfectly clear on the following points: The selection of oxygen as the standard of comparison and the assigned combining weight as 16 is purely arbitrary and is decided solely by convenience. Any other element and any other value could be taken and the relative values would be the same. The equivalent weights are determined directly by analysis or synthesis of compounds, using oxygen taken at 8 as the standard of comparison. The selection of the combining weights which we use in the following pages rests upon facts and hypotheses which are discussed in Chapter V. The student should be clear also on the following points: Combining weights are **any** set of numbers in terms of which the composition of compounds may be expressed. Equivalent weights are that particular set which represents the weights of elements found in combination with 8 of oxygen. The atomic weights are a **selected set** of numbers with oxygen 16 as a basis.

**Symbols.** — Since each element has its own combining weight, it is convenient at times, in the interest of brevity and clearness, to use symbols which represent not only abbreviations of the

names of the elements, but also the atomic weights. Thus the symbol, O, is used for oxygen and represents 16 parts by weight of the element. Similarly, H indicates hydrogen and represents 1.008 parts by weight of hydrogen. This use of symbols we owe to the Swedish chemist, Berzelius, and it doubtless grew out of the secret cabalistic signs of the alchemists. (See Mellor, *Modern Inorganic Chemistry*, p. 38.) By reference to the table of atomic weights, it will be seen that the symbols are variously derived. In many cases the first letter of the name of the element is used alone; where this would not be distinctive the second or some other letter is used. Thus the symbols Cl, Br, Ca, etc., represent atomic weights of the elements chlorine, bromine, calcium, etc. The symbols which were first used were derived from the Latin names of the elements, but some of the more recent elements have symbols derived from the English or German names. Thus, Na (natrium), Cu (cuprum), K (kalium), Fe (ferrum), W (wolfram) etc., are the symbols used for atomic weights of the elements sodium, copper, potassium, iron, tungsten, etc.

It is interesting that the symbols used in chemistry are the same in all languages, with the single exception of the symbol Az (Azote), used by the French, where other languages use the symbol N for nitrogen. This seems due to an ill-placed reverence for Lavoisier, the great French chemist. (See Chap. II.) Chemistry and music have, therefore, in a sense, a universal language.

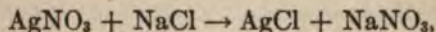
The student is confused at times by the abstract character of the atomic weights. The symbol O represents 16 parts by weight of oxygen. How much oxygen does it stand for? The atomic weights are purely relative. The atomic weight of an element may be expressed in any unit of weight in which the element or elements with which it is compared are expressed. The symbol O represents 16 grams, ounces, pounds, or tons of oxygen whenever oxygen is compared with 23 grams, ounces, pounds, or tons of sodium, etc.

**Formulae.** — If we wish to express the composition of a compound by means of symbols, it is the chemical convention to write the symbols immediately after each other, using subscripts where more than one atomic weight is represented. Thus: NaCl expresses the composition of common salt, since it consists of 23 parts by weight of the element sodium and 35.45 parts of chlorine. Again,  $\text{Cu}_2\text{O}$  means that in the compound cuprous oxide, for every 16 parts of oxygen there are  $2 \times 63.6$  of copper. CuO represents the composition of the black oxide of copper and  $\text{PbCl}_2$  of lead chloride. These combinations of symbols are known as formulae.

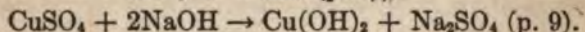
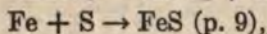
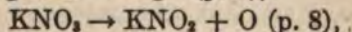
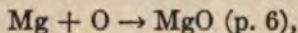


The value of the atomic weights and the symbols representing them will now begin to be apparent to the student. The method by which the formulæ are obtained will be illustrated from time to time in subsequent pages. In the laboratory the student will be called upon to perform, in a few instances, the necessary experimental steps and calculations.

**Equations.**—By means of symbols and formulæ it is very frequently possible to represent chemical changes very briefly and clearly, so that a glance will convey information it would take many words to express. To illustrate: If we take silver nitrate, which we know to be composed of one atomic weight of silver (symbol  $\text{Ag} = 107.92$ ), one atomic weight of nitrogen ( $\text{N} = 14$ ) and three atomic weights of oxygen ( $\text{O} = 16$ ), and treat this with common salt, which consists of one atomic weight of sodium ( $\text{Na} = 23$ ) and one atomic weight of chlorine ( $\text{Cl} = 35.45$ ), we obtain as a result silver chloride consisting of one atomic weight of silver ( $107.92$ ) and one of chlorine ( $35.45$ ) and sodium nitrate consisting of one of atomic weight each of sodium ( $\text{Na} = 23$ ) and nitrogen ( $\text{N} = 14$ ) and three atomic weights of oxygen ( $\text{O} = 16$ ). This long and somewhat complicated statement is all embraced in the equation



where the sign  $+$  indicates the interacting materials and the  $\rightarrow$  the direction of the change. This equation should be read: Silver nitrate and sodium chloride give silver chloride and sodium nitrate. In a similar manner we may express some of the chemical changes we have encountered:



This method of expression of chemical change is of great value, but it is extremely important that the student understand its limitations at the beginning. The equation is algebraic in form only. The left side of the equation gives no indication of how the right side is obtained. The right side represents the same quantity of material as the left, since the law of conservation of mass obtains. There is no intimation that all the substances

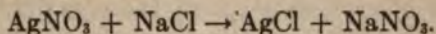
represented on the left are converted to the substances on the right, but only that in so far as they are converted the quantitative relations indicated hold true. There is also no intimation of the conditions needed to produce the change. For example: In the equation first given there is nothing to indicate that the substances must be in solution in order that the reaction may take place, yet such is the case. In every equation we must by some means know both sides of the equation before it may be written. When occasion arises we shall enter more into detail regarding the method of forming the equation. In the equation last given above it will be noted that the formula of sodium hydroxide, NaOH, has a prefix, 2. This means that when copper sulfate is treated with sodium hydroxide under such conditions that copper hydroxide is formed, two formula weights of sodium hydroxide are required for each formula weight of copper sulfate. By the term "formula weight" is meant the sum of the atomic weights of the elements represented in the formula. The formula weight of copper sulfate is, therefore,  $63.6 + 32.06 + (4 \times 16) = 159.66$ . That of sodium hydroxide is  $23 + 16 + 1.008 = 40.008$ . The equation then states that the relative quantities of copper sulfate and of sodium hydroxide required to produce copper hydroxide and sodium sulfate are as 159.66 to 80.016.

**Arithmetical Calculations.** — In the chemical laboratory we frequently desire to know how much material must be used to produce a definite quantity of a given substance, or how much material may be produced by a decomposition or by an exchange of known character. In such calculations we invariably use the metric system of measures and if the student is not sufficiently familiar with these measures, so that he forms mental pictures of them when mentioned, he should lose no time in becoming familiar with them. A table of metric measures and their English equivalents is given in the Appendix. Two typical examples of the methods employed may be given.

If 20 grams of iron are to be completely transformed into iron sulfide, how much sulfur will be used and how much iron sulfide will be produced? We must first know, or determine, that the compound has the composition expressed by the formula FeS, i.e., the equation  $\text{Fe} + \text{S} \rightarrow \text{FeS}$  represents the chemical change. The combining weights are Fe = 56, S = 32, therefore  $56 : 32 :: 20 : x$ ; or  $32/56 \times 20 = 11.43$  g., the amount of sulfur required. Since



the formula weight of FeS is 88, therefore  $56 : 88 :: 20 : x$ , or  $88/56 \times 20 = 31.43$  g. sulfide is formed. In the reaction between silver nitrate and sodium chloride the composition of the reacting substances is known and the nature of the change when they interact; therefore, if the question is how much silver nitrate is required to react exactly with 10 grams of sodium chloride, we first set down the equation



Since the formula weight of the nitrate is  $(107.93 + 14 + 3(16)) = 169.93$  and of sodium chloride  $(23 + 35.45) = 58.45$ , therefore  $169.93 : 58.45 :: x : 10$ , or  $169.93/58.45 \times 10 = 29.073$  g.; the amount of silver nitrate required. It is apparent also that it is equally easy to find the quantity of silver chloride (AgCl) and of sodium nitrate ( $\text{NaNO}_3$ ) formed from these quantities of silver nitrate and of salt.

**Summary.** — In this chapter we have attempted to make clear the following points: The science of chemistry is a dependent part of science in general. We may with some advantage classify the various forms of matter under the heads: elements, compounds, mixtures, solutions. We may consider the changes we observe as either chemical or physical. Chemical changes are described as always abrupt and accompanied by such material alteration of the properties of the substances changed that their identity is destroyed. There are but four **types** of chemical change. The law of conservation of mass obtains with chemical changes as well as with physical changes. The laws of definite proportions, of multiple proportions and of combining weights describe the weight relations of chemical changes in such manner that we are able to express the weight relations of the elements in compounds by means of definite formulæ, and of chemical changes by means of equations.

These matters have been presented not dogmatically, but with the purpose of showing how and why they were developed. If the student has had no previous experience in chemistry he may find the discussion dry. He may also fail to see very clearly how the knowledge of these points will be helpful. He may, however, rest assured that they are fundamental parts of the machinery by which he may ultimately hope to gain control over a vast and useful, as well as beautiful, portion of the field of science.

**Exercises.** — 1. Define a science. Explain how knowledge may be unscientific. Why is science subdivided? Why are the boundary lines of a given branch of science indistinct? Why is chemistry subdivided?

2. Define the word element. What were the Aristotelian elements?

3. How are the various changes which matter undergoes classified? In the interval between the beginning and the end of a physical change in a given portion of matter what occurs?

4. Make a list of ten changes you have observed in the previous twenty-four hours, classify them as physical or chemical, and give your reason for each assignment.

5. In a sawmill one may observe the following changes: motion of logs and lumber, heating of boilers and engines, formation and condensation of steam, burning of waste wood, distribution of gases through the atmosphere, rusting of iron, and drying of wood. Which of these involve physical, and which chemical changes? Explain your answer.

6. Cite three natural laws and three mandatory laws.

7. Take a text-book on chemistry and select from the chemical changes there described, three which are decompositions, three syntheses, three exchanges.

8. Select a chemical change which goes on in your room, kitchen, basement, barn or garage and state from what properties you infer the change to be chemical.

9. Distinguish between fact and law. State some law and tell why it is a law. Of what use are laws in science?

10. Express the composition of the following compounds in terms of atomic weights or their integral multiples: cupric oxide, cuprous sulfide, mercuric chloride, hydrogen sulfide.

11. If a compound has the composition shown by the formula  $\text{FeCl}_2$ , how much iron would be required to make one pound of it? How many grams of chlorine in 50 grams of the compound?

12. If the equation,  $\text{Fe} + \text{S} \rightarrow \text{FeS}$ , represents the reaction between iron and sulfur in forming iron sulfide, how many grams of iron are required to form 20 g. iron sulfide?

13. Show how the following analyses of three oxides of nitrogen illustrate the Law of Multiple Proportions:

	A	B	C
Nitrogen . . . . .	63.65	46.68	25.94
Oxygen . . . . .	36.35	53.32	74.06

14. Two oxides of a metal contain 22.53 and 30.38 per cent oxygen. If the formula of the first oxide be  $\text{MO}$ , what will be that of the second?

15. The following table contains the analyses of a list of compounds. Starting with oxygen as 8, calculate the equivalent weight of the other elements.

	Per cent.	Per cent.
Water:	Hydrogen....11.18,	Oxygen.....88.81.
Hydrogen chloride:	Hydrogen.... 2.76,	Chlorine.....97.23.
Silver chloride:	Silver.....75.25,	Chlorine.....24.74.
Sand:	Silicon.....46.93,	Oxygen.....53.07.

16. State in words the information conveyed by the symbol " $\text{Cl}$ "; by the formula " $\text{NaCl}$ "; by the equation,  $\text{FeCl}_2 + \text{Zn} \rightarrow \text{ZnCl}_2 + \text{Fe}$ .

What weight of zinc will displace 50 g. of iron in the above interaction?



## CHAPTER II

### OXYGEN

**Introduction.** — The study of the elements and their compounds may be begun with any element we choose, yet there are many reasons which lead us to select oxygen as the starting point. It is an element which is found both free and combined. It combines with almost all the other elements, and its compounds are the commonest substances. It can be prepared in a pure state easily and cheaply and its preparation is easy for beginners. The experiments which illustrate its behavior are easily performed, are strikingly interesting and may be made very spectacular. The history of modern chemistry begins with the discovery of oxygen, and by common consent it has been made the fundamental element of the chemical system. For these reasons, as well as many others, we may begin our systematic study of the elements and their compounds with oxygen. In its study, as with all other elements, we shall pursue the plan of presenting the subject matter under the sub-heads, Occurrence, History, Preparation, Physical Properties, Chemical Properties, Uses and Compounds. Under these sub-heads, we will also present such generalizations as are specially illustrated by the element under consideration, or as are needed for the satisfactory presentation of the topic under discussion. As material offers, and the development of the subject demands, special chapters dealing with the methods of work, with hypotheses, and with generalizations, will be introduced. These will be presented only after the need for them is felt.

**Occurrence.** — Oxygen is found free in the air, mixed with a larger amount of nitrogen and small amounts of many other substances. 20.8 per cent by volume and 23.1 per cent by weight of dry air is the free element. Water is 88.8 per cent oxygen. Sand and clay when pure are about 53 per cent oxygen and in many siliceous rocks the percentage is nearly as great. Limestone is 48 per cent oxygen. It follows then that bricks, mortar, cement,



plaster, etc., are largely oxygen. Vegetable substances frequently contain oxygen, 50 per cent to 70 per cent. The human body is approximately 66 per cent oxygen and those of other animals contain the element to a similar extent. Many manufactured articles also frequently contain large quantities of this all but omnipresent element.

**History.** — The important part played by oxygen in the development of chemistry cannot be fully appreciated at this stage. As the subject is developed this will become increasingly apparent. A short discussion will at least be interesting and perhaps stimulating. For many centuries the air was considered an element. (See p. 3.) In 1774 Priestley (see Thorpe's Chemical Essays and Alembic Club Reprint, No. 7), an English minister, became interested in the substances produced by heating various bodies,

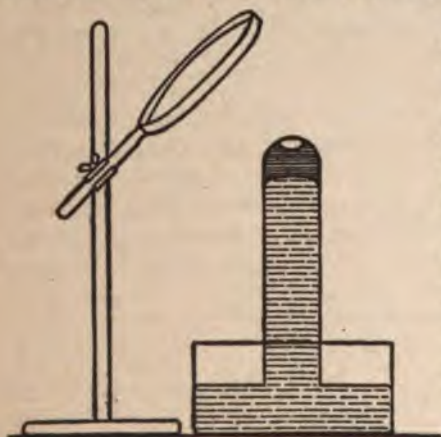


FIG. 3.

in closed vessels, by means of a lens. (Fig. 3 shows the character of his apparatus.) Among other things so heated was the substance known as mercuric oxide. This he knew by the name "*Mercurius Calcinatus per se.*" When this was confined above mercury in a glass vessel and the heat of the sun's rays concentrated upon it by means of the lens, a very large amount of "air" or gas was formed. This gas was upon investigation found to support combustion more readily than ordinary air and

a mouse lived in it longer than one could in the same amount of air. Scientists at the time very generally held the phlogistic\* theory to be

\* The Phlogistic Hypothesis. The remarkable fact that ordinarily when substances burn something seems to escape from the burning body, as evident from the upward rushing of the flame, led to the gradual development of the phlogistic hypothesis, which is usually credited to Becher (1635-1682) and Stahl (1660-1734). Substances were supposed to be combustible because they contain a factor, phlogiston, which escapes during combustion. The air already contains some phlogiston from previous combustions, but can take only a limited amount, hence, if a

see below) and Priestley, therefore, failed to recognize the simple form of matter, but considered it as air from which phlogiston had been extracted. He called it "dephlogisticated

about the same time, Scheele, a Swedish scientist, also discovered that oxygen could be obtained by heating various substances including potassium nitrate and manganese dioxide, but his work was not published so soon as, nor did it have the same far-reaching results as, Priestley's. Lavoisier, a French scientist, learning of Priestley's work, was able to show that phlogiston could be converted to ash, i.e., calcined or rusted metal, in the air, and that at the same time some of the phlogiston appeared. The apparatus shown in Fig. 4. The portion of the air which would not support the mercury was inca-

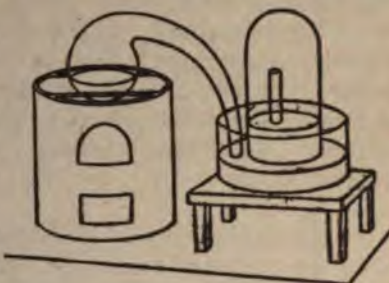


FIG. 4.

supporting combustion or respiration. He called this residue "air" (from  $\alpha$  = not and  $\zeta\omega\rho\acute{o}s$  = living). By heating the calcined metal to a higher temperature the portion of the air which had been absorbed was regained. Priestley's air is, therefore, one of the constituents of ordinary air and combustion consists in the union

of the metal with phlogiston. If a substance is burned in a limited amount of air the combustion stops when the air is saturated with phlogiston just as water dissolves salt to a certain extent and, when saturated, solution ceases. It was known, of course, that certain substances, such as iron, etc., increased in weight on being burned, but this was met by the phlogistic theory by assuming phlogiston to be a principle of levity, i.e., to have a negative weight. This hypothesis was offered as an explanation of combustion and from it terms were derived such as above given for oxygen. (See also hydrogen.) (For an account of Phlogiston see Rodwell, Phil. Mag., 1868.)

The above explanation, incorrect as it is, is given partly because of its historical interest, but also as an interesting example of what is known as an explanation in terms of the phlogistic theory, the air obtained by Priestley was designated, i.e., it was air from which phlogiston had been removed and by consequence it could take up more phlogiston than could the same quantity of ordinary air. It will be seen that this is simply a statement in some detail of the behavior of Priestley's air. This is all an explanation is, and, as such, it may easily be incorrect. What we believe to be a correct explanation of the process of combustion is that furnished by Lavoisier (*vide infra*).



of this substance with the materials burned. Lavoisier proposed that the element be called oxygen (from  $\acute{o}\xi\acute{\upsilon}\varsigma$  = acid and  $\gamma\epsilon\nu\eta\varsigma$  = producing), because he **supposed** it to be essential to the formation of acids. This explanation of combustion, together with other contributions of Lavoisier, gave such stimulus to chemical study and at the same time furnished a more precise basis for classification, that chemistry is sometimes said to have been founded by Lavoisier.\* In presenting the above facts the student is not to infer that the existence of oxygen was first noted by Priestley. It had been previously prepared by others. Its existence and relationship to air were known to the Chinese even centuries ago. It was, however, Priestley's discovery which became effective in promoting the development of the subject. It is usually the observation that produces subsequent development which is regarded as a discovery.

**Preparation.**—The individual processes for the preparation of oxygen are very numerous. Below are given certain **methods**. Each method may include several processes of like type.

1. **From the Air.** Since oxygen is present in the air in such large quantities, the air might be expected to be the most convenient source from which to obtain it in the pure state. This is not the fact. However, if air is converted to the liquid state (*cf.* p. 278) and is then allowed to evaporate, since the other components of the air are more or less volatile than oxygen by selecting the proper fraction of the vapor and collecting it in suitable vessels nearly pure oxygen may be obtained. This process requires rather elaborate and expensive apparatus and also considerable skill and experience on the part of the operator. It is not used in small scale operations. Also when air is dissolved in water the amount of oxygen dissolved is relatively greater than the proportions found in air. The dissolved gases may be extracted from water by means of an air pump and the operation repeated. In this manner nearly pure oxygen has been obtained. This process is impractical.

2. **From Water by Electrolysis.** If water is slightly acidified it becomes a good conductor of the electric current, and when the current is passed through the solution, the result is, in effect, the separation of the water into its constituent elements, hydrogen and

\* Lavoisier's life was full of incident and fruitful of consequence and had much of romance and tragedy. The student will enjoy reading *Heroes of Science*, pp. 79-105, and Thorpe's *Chemical Essays*, p. 123.

oxygen, though this is by no means the whole story connected with the operation. One form of the apparatus used is shown in Fig. 5. The gas produced in smaller volume is oxygen and may be collected. This method is in use for the preparation of oxygen for commercial purposes, but is not the most convenient method for laboratory preparation.

**3. From Oxygen Compounds by Heating Them.** Substances which contain oxygen may be decomposed by heat and, under proper circumstances, the oxygen so liberated may be conveniently collected. The substance most commonly used for the purpose is potassium chlorate ( $\text{KClO}_3$ ), which contains approximately 39 per cent oxygen, all of which may be liberated by a rather small increase of temperature ( $351^\circ \text{C.}$ ). A convenient form of apparatus is shown in Fig. 6. While the statement at the opening of this paragraph is doubtless true, it must not be inferred that it is of no consequence what oxygen compound is heated. Oxygen is liberated from certain compounds at or below the ordinary temperature, *i.e.*, the substances are only to be had at low temperatures. Other substances require such very high temperatures as to be beyond the range of an ordinary heating device. Thus with an ordinary burner oxygen may be obtained by heating barium dioxide, potassium nitrate, manganese dioxide, etc. The temperature attained by means of a blast lamp is required for the decomposition of potassium bichromate. Other substances such as sand must be heated to a still higher temperature before oxygen is liberated. This is the ordinary laboratory method.

Which substances may be used as a source of oxygen is determined also by other considerations than the temperature required. The substance may be so expensive as to cost more than the value of the products. The other products of the decomposition may be of such character as to be undesirable and render the collection of the oxygen difficult. The material used may be such as to render breakage or destruction of the apparatus probable. In general, the choice of materials serving as possible sources of the

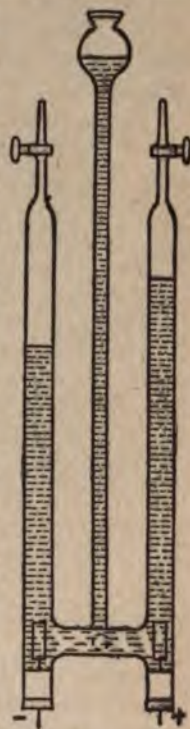


FIG. 5.



gas is determined by economy in cost of production, taking into account raw materials, time, energy, convenience, cost of apparatus, labor, etc.

4. **Special Processes.** Two special processes for the preparation of oxygen may be given, Brin's process and the oxone process.

If the substance barium oxide,  $\text{BaO}$ , is heated to about  $500^\circ \text{C}$ . in a current of air, it takes up oxygen and is converted into barium peroxide,  $\text{BaO}_2$ . This fact may be expressed equationwise:  $\text{BaO} + \text{O} \rightarrow \text{BaO}_2$  (1). If now the peroxide be heated to upwards of  $700^\circ \text{C}$ ., oxygen is liberated and the barium oxide again formed. That is,  $\text{BaO}_2 \rightarrow \text{BaO} + \text{O}$ . Indeed it is found that if the apparatus is maintained at  $700^\circ$  and air is pumped in at about 30 pounds pressure the reaction goes as indicated in equation (1). If when this reaction is complete the air current is shut off and a suction pump is applied the oxygen is given off and may be pumped into cylinders. The equation,  $\text{BaO}_2 \rightleftharpoons \text{BaO} + \text{O}$ , may be written to express Brin's process.

The oxone process makes use of sodium peroxide,  $\text{Na}_2\text{O}_2$ , and water. The reaction takes place at the ordinary temperature when water is brought into contact with the peroxide. The reaction may be indicated by the equation  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{O}$ . This process is the one usually employed to furnish oxygen for the use of physicians and for "lung motors" (*vide Uses*).

**Catalytic Action.** — When potassium chlorate is heated alone, it melts and oxygen begins to come off only when a temperature above the melting point is reached. Manganese dioxide does not give oxygen until heated to  $400^\circ \text{C}$ . or above. If, however, a little manganese dioxide is mixed with the potassium chlorate, the mixture begins to give oxygen before  $200^\circ \text{C}$ . is reached, and all the oxygen of the chlorate may be removed at that temperature, while the manganese dioxide may be regained unchanged after the operation. Such behavior is not uncommon in chemical reactions, and, indeed in the present case, the decomposition of the chlorate may be facilitated by the presence of lead peroxide, ferric oxide and other substances.

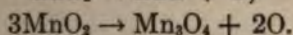
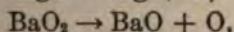
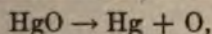
Such a reaction as that above described is known as a catalytic action, and the process as catalysis. The added substance is called a catalytic agent or a catalyzer (from *κατά* = down and *λύσις* = the act of loosing). A catalyzer may be defined as a sub-

stance which affects the speed of a chemical change without itself being *permanently* affected by the change.

This subject will be more fully discussed later, but the attention of the student should be called to the form of the above statement. A catalyzer may be either retarding or accelerating in its action and in some cases the exact mode of its action may be known. Thus catalysis is not necessarily a mystery, as is so often the view of it held by both student and teacher.

**Making an Equation.**—In order to properly express the chemical changes discussed in the preceding paragraphs by means of equations, we must first know the exact composition, *i.e.*, formula, of the substances decomposed (*vide infra*). We must also know exactly what the products are and how much of each. If the composition of potassium chlorate is correctly given by the formula  $\text{KClO}_3$ , and we find upon investigation that all the oxygen may be liberated by heating and that the residue is a substance known as potassium chloride, with the composition shown by the formula  $\text{KCl}$ , we may then write the equation  $\text{KClO}_3 \rightarrow \text{KCl} + 3\text{O}$ .

Similarly, when the necessary facts are in our possession, we may write the other changes mentioned as follows:



It will be observed that both sides of the equation must be known. The ultimate source of this information is the laboratory through quantitative experiment, though of course if the results of such experiments are embodied in text-books or scientific memoirs, we may gain the needed information, if we but know where to look, without *personal* appeal to the laboratory. The point to be especially emphasized here is that only in the laboratory could it be discovered that the products of heating manganese dioxide are oxygen and a compound having the formula  $\text{Mn}_3\text{O}_4$ , and, therefore, at least three formula weights of manganese dioxide must be decomposed to produce one formula weight of the "manganous manganic oxide" ( $\text{Mn}_3\text{O}_4$ ), or hausmannite.

**Physical Properties.**—In the preceding discussion, no mention has been made, except in connection with Priestley's experiment, of the properties of this element.



If the apparatus shown in Fig. 6 is used for heating a mixture of potassium chlorate and manganese dioxide and the delivery tube is placed beneath the mouth of a vessel filled with water and inverted in the pneumatic trough ( $\pi\nu\epsilon\upsilon\mu\alpha$  = air), the oxygen, as given off, will displace the water. At first the gas may appear more

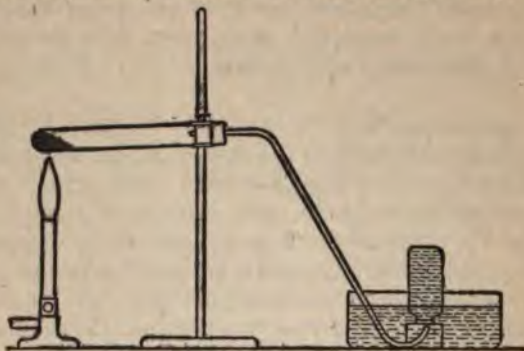


FIG. 6.

or less foggy, but this is due to solid particles carried over mechanically by the rush of gas from the generator. After standing for a time, this cloud will disappear and the gas will be observed to be completely colorless. Further investigation reveals the fact that it is also tasteless and odorless. These and other important physical properties of oxygen are listed in the following table. The student who has had but little training in physics will not see the significance of all the properties listed and the discussion of some of them is deferred to subsequent chapters.

1. Colorless.
2. Odorless.
3. Tasteless.
4. Solubility in water, 4 cc. to 100 at  $0^{\circ}$  C.
5. Color in liquid state, pale blue.
6. Boiling point,  $-182.5^{\circ}$  C.
7. Melting point,  $-227^{\circ}$  C.
8. Specific gravity (air = 1), 1.105.
9. Density (H = 1), 15.96.
10. Weight of 1 liter = 1.429 grams.
11. Specific gravity of liquid (water = 1), 1.13.
12. Critical pressure, 50 atmospheres.
13. Critical temperature,  $-118^{\circ}$  C.



**Solubility.** — It will be observed that while oxygen is not wholly insoluble in water, yet it may be collected over water without serious waste. This is especially true because, as is generally true of gases, the solubility decreases with increase of temperature, becoming nil at  $100^{\circ}\text{C}$ . At room temperature,  $15^{\circ}$  to  $20^{\circ}$ , the solubility is from 3.4 to 3 cc. per 100 cc. of water. The amount of oxygen present as dissolved gas in ordinary water is much less than the figures given. When any gas is dissolved in water the quantity dissolved varies as the pressure of the gas (Henry's Law). Also, in a mixture of gases each gas dissolves independently of the others present. Consequently, water may dissolve only one-fifth the quantity of oxygen from the air which may be dissolved from an atmosphere of pure oxygen. Ordinarily, also, water is not completely saturated with air. Nevertheless this amount (less than from 0.6 to 0.7 cc. per 100 cc. of water) is all-important to sub-aquatic life, since fishes and subaquatic plants respire oxygen and use this dissolved gas in their respiratory processes.

**Gas Measurement.** — The relative weight of different gases is frequently expressed by comparing them with a standard gas. The most frequently used standard of comparison is air. If we were to determine the weight of a given volume of oxygen and compare this weight with that of the same volume of air under the same conditions we would find the ratio of the weights to be 1.105 to 1. The relative weights of gases compared with air as unity is termed the specific gravity of gases. The chemist not infrequently wishes to compare the weight of a given gas with another standard, *e.g.*, with hydrogen. Thus the density of oxygen is 15.96 times that of hydrogen under the same conditions. Since the gases change in volume with change either of temperature or of pressure, if we wish to express the weight of a definite volume of any gas we must specify the temperature and pressure under which the gas volume is measured. By convention gases are assumed to be weighed at a temperature of  $0^{\circ}\text{C}$ . and a pressure equal to that exerted by a column of mercury at  $0^{\circ}\text{C}$ . and 760 mm. in length. These are known as standard conditions. Thus, when we say that a liter of oxygen weighs 1.4290 grams we imply, whether we state it or not, at standard conditions. Since  $0^{\circ}$  is an inconvenient temperature at which to work and since also gases are usually measured over mercury or water at pressures which balance the atmospheric pressure, which is seldom at the standard value, the ordinary practice is to measure the volume of a gas at whatever temperature or pressure is convenient and then calculate the volume it would have at standard conditions. This calculation involves certain principles which are a part of every course in elementary physics but are here given for the sake of completeness. (For fuller treatment consult text-books on physics.)

**Boyle's Law.** — Boyle (1660) made the observation that gases all behave similarly toward change in pressure, the temperature being constant. The rule

may be variously stated. The volume of gas varies inversely with the pressure, or in other words, the volume times the pressure is a constant, or again, the concentration of a gas varies directly with the pressure upon it. It follows that if a gas is measured at some pressure other than the standard pressure, the volume under standard pressure may be found by multiplying by the ratio of one pressure to the other. An example: Suppose we have a volume of gas which occupies 50 cc. at atmospheric pressure and the corrected barometer reading (see below) is 748 mm. Then at 760 mm. the volume will be  $748/760 \times 50$  equals 49.2 cc. It will be seen that to find the volume at a given pressure when the volume at any other pressure is known it is only necessary to multiply by this ratio. To determine which number is the numerator it is only necessary to consider whether the volume will increase or decrease, because of the change. To illustrate again: If a gas volume is 100 cc. at 770 mm., its volume at 720 mm. is  $(770/720 \times 100)$  106.94 cc. The Law of Boyle is also known as Mariotte's Law because it was discovered independently by Mariotte in 1677.

**Charles' Law.** — In 1737, Charles, a Frenchman, reached a conclusion with regard to the change of gas volume with change of temperature, which observation was also independently made by Dalton and Gay-Lussac (1802) and by them brought into general recognition. It is sometimes known by the name of Gay-Lussac's Law. It may be stated: The pressure remaining constant, gas volumes vary  $1/273$  of their value at  $0^\circ \text{C.}$  for every change of one degree centigrade. It will be observed that if this rule should hold rigidly for all temperatures all gas volumes would become zero at  $-273^\circ \text{C.}$  This temperature is, therefore, called the absolute zero, and we may reckon the changes on this scale. So long as gases obey this rule their volumes vary directly as the absolute temperature, the pressure remaining constant. Temperatures on the centigrade scale may be converted to absolute readings by mere addition of  $273^\circ$ . This furnishes the most convenient method of converting observed gas volumes to standard conditions when measured at any other temperature. To illustrate: If a gas volume is 100 cc. at a temperature of  $15^\circ \text{C.}$ , it becomes on cooling to  $0^\circ$  ( $273/288 \times 100$ ) 94.8 cc., or a gas volume of 100 cc. at  $-10^\circ \text{C.}$  becomes at  $20^\circ \text{C.}$  ( $293/283 \times 100$ ) 111.4 cc. Since the influence of temperature and pressure upon gas volumes are independent functions, both corrections of gas volume may be applied independently and, therefore, if we wish to find the volume of any gas at standard conditions when measured under other conditions it is only necessary to successively make application of these two principles. Thus, if we desire the volume under standard conditions of a gas volume measuring 100 cc. at a temperature of  $75^\circ \text{C.}$  and 740 mm. pressure we have:  $100 \times 273/348 \times 740/760 = 76.4 \text{ cc.}$

**Water Vapor Correction.** — Since gases are frequently measured over water and water vapor is formed and occupies a part of the space apparently occupied by the gas, it is necessary to make correction for this in work which is at all accurate. To illustrate: In Fig. 7 we have, let us say, 100 cc. of oxygen at atmospheric pressure, since were it not at atmospheric pressure the water would either be forced up the tube perhaps to A by the outside pressure if greater, or



down to *B* were the inside pressure greater. Since, however, it stands at *C*, we can learn the pressure of the gas by referring to a barometer which records the pressure of the air, and, therefore, of the 100 cc. of gas in the vessel. Not all the gas present is oxygen, since some water vapor is mixed with it. Were this withdrawn and no more allowed to enter, clearly the pressure on the outside would be the greater and water would be forced into the tube. The pressure of water vapor under such circumstances is a function of the temperature only, and in the Appendix will be found a table showing this pressure (aqueous tension) for temperatures from 0° C. to 100° C. It will be obvious that if we wish to obtain the pressure due to the oxygen alone it is only necessary to subtract from the observed barometric reading the aqueous tension for the temperature at which the measurement is made. Therefore, 100 cc. of a gas at 15° C. and 740 mm. measured over water will, if dry, occupy a volume under standard conditions found as follows:

$$100 \times \frac{740 - 12.7}{760} \times \frac{273}{288} = 90.26 \text{ cc.}$$



FIG. 7.

**Correction for Barometric Reading.**—In stating standard conditions the standard pressure is 760 mm. of mercury at 0° C. Mercury expands on being warmed and it is, therefore, clear that the pressure of a column 760 mm. in length at 15° C. is not the same as at 0° C. While the observed barometric readings are not very different from what they would be were the barometer kept at 0° C., yet in very accurate work this correction also must be kept in mind in order to convert the barometric reading at room temperature to the value at 0° C. It will be noted that this value is also to be subtracted from the observed barometric height. If the barometer were also at 15° C., therefore, in the above case,

$$100 \times \frac{740 - 12.7 - 2}{760} \times \frac{273}{288} = 90.07,$$

the volume of the oxygen under standard conditions. (For a table of barometric correction values see Appendix.)

**Chemical Properties.**—The chemical properties of a substance include, the list of other substances with which it interacts chemically, the character of the substances produced, the various types and conditions of reaction, the speed of reaction and the energy relations involved. In a description of the chemical properties of an element ordinarily only the more important properties are given.



**Direct Union with Elements.**—Oxygen unites more or less readily with all the other elements except fluorine and bromine and the group of inactive elements known as the argon family (*vide* p. 275). The products are called oxides. A few illustrative examples of the direct union of oxygen are described: If a small amount of red phosphorus is placed in a deflagrating spoon (A in Fig. 8) and heated until it begins to burn and then is plunged into a vessel of oxygen, it will burn more vigorously than in air, with an intense white light and with the formation of a white cloud. The cloud consists of particles of a white solid which will

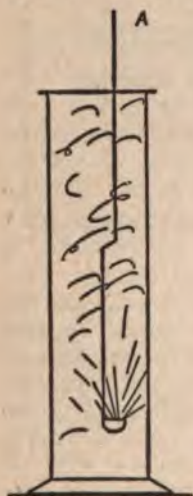


FIG. 8.

gradually settle upon the walls and bottom of the vessel. If water is present, or is subsequently added, the solid dissolves to make a liquid (a solution) which will change blue litmus (paper or solution) to a pink color. This change in litmus is characteristic of a class of bodies called acids, and hence we may say that the product formed by burning phosphorus in oxygen, when dissolved in water, forms an acid. The same substance is produced, though less rapidly, when phosphorus is burned in air. If sulfur is heated in the same manner and plunged into oxygen it burns with increasing vigor and a weird bluish light. In this case no heavy cloud is formed, but a choking, ill-smelling gas is produced. The odor belongs neither to the sulfur nor to the oxygen, though it is at times called the "odor of sulfur." The ill-smelling gas dissolves quite rapidly if shaken with water

and the solution is an acid as indicated by the reddening of litmus when the latter is added. If charcoal (the element carbon) is heated to redness on a spoon and placed in oxygen, it glows with an increased brightness, and the product of reaction, as with sulfur, is a gas with only a slight and not unpleasant odor. When this gas is shaken with water, it is dissolved and forms an acid. In this case the acid formed will not render litmus distinctly red, but will destroy the color of a red solution of phenolphthalein, which also is a typical action of acids. It was such reactions as these which led Lavoisier to the erroneous conclusion that all acids contain oxygen as an essential constituent.

If sodium be similarly treated it burns with a yellow flame,

and if the product is dissolved in water, a soapy bitter solution is obtained which turns red litmus blue and produces a pink color in a colorless solution of phenolphthalein. This behavior is characteristic of a class of substances called bases. Several other elements behave in an analogous manner.

If steel wool is heated in a Bunsen burner until it begins to burn, and is then plunged into a vessel of oxygen, it burns brilliantly, producing a shower of sparks. If the effort is made to dissolve the product of this reaction in water, the result is negative. Similarly, the products from the burning copper, tin or lead in oxygen are insoluble in water.

If the reactions described are carried out experimentally, it will be seen that with certain elements oxygen is extremely active at elevated temperatures. That is to say, chemical reaction takes place rapidly. It will be noted also that the products, oxides, are of three general types: (a) soluble in water, producing acids, (b) soluble in water, producing bases, (c) insoluble in water. The substances which are above described as uniting rapidly with oxygen at higher temperatures will, for the most part, remain in air or even in pure oxygen, at the ordinary temperature, without evidence of reaction. We know, however, that iron rusts, *i.e.*, forms an oxide slowly, in moist air. The same sort of reaction also takes place with other elements. We may say then that oxygen is comparatively inactive at ordinary temperature.

**Indirect Union with Elements.**—Certain elements will not unite with oxygen at either ordinary temperatures or when heated with it. In some cases, however, oxides of these elements may be obtained indirectly; *e.g.*, if lead nitrate is heated sufficiently, an oxide of nitrogen is produced. We may heat nitrogen with oxygen at even a comparatively high temperature without any evidence of direct union. (See, however, p. 292.) Other examples of oxides obtained by indirect methods are those of silver and of chlorine.

**Reaction with Compounds.**—Frequently compounds will react chemically with oxygen, *e.g.*, we may burn kerosene, turpentine, wood, sugar, etc. With some substances this type of reaction may take place even at ordinary temperature, under special conditions. Wood, for example, slowly decays, *i.e.*, reacts chemically with oxygen when exposed to air and moisture. It burns, *i.e.*, unites rapidly with oxygen when heated in the air or in pure oxygen. A case of special interest is the reaction within



the animal body between oxygen and the animal tissues. Oxygen, absorbed through the lungs, is able to react with the tissues of the body and produce not only the heat needed to maintain the body temperature, but to convert the worn out material into forms which are readily removed from the body. The discussion of such chemical changes forms a very important part of physiological chemistry.

In order to describe more precisely the chemical relations of oxygen it is necessary to discuss the following: the making of formulas to express exactly the composition of the substances produced, the making of equations for concise expression of the changes, the influence of temperature, and the energy relations which accompany the mass changes. These will, therefore, be presented at this point. It should be emphasized that the principles involved are common to all chemical reactions.

**Making of Formulas and Equations.** — In order to determine more exactly what are the substances produced when oxygen

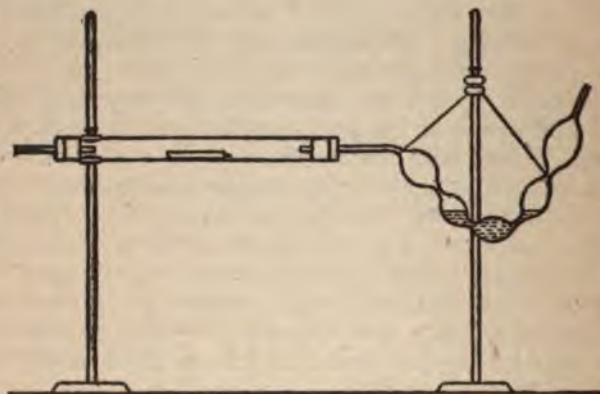


FIG. 9.

unites with carbon, phosphorus, etc., we might proceed somewhat as follows: A hard glass tube about 18 inches in length is provided with two one-holed rubber stoppers to fit. Each stopper carries a small glass tube. Into a small porcelain boat weigh carefully a half gram of pure carbon and insert the stoppers. Support the whole so that the boat may be heated by a Bunsen



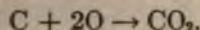
burner. When hot, pass a slow stream of oxygen over the charcoal and collect the products in a weighed series of bulbs, containing caustic potash solution, known as Liebig bulbs. The whole apparatus is shown in Fig. 9.

After all the carbon is burned and the product swept out by means of the oxygen, the caustic potash bulb is again weighed and the increase noted. If we now have results as follows: Carbon 0.500, increase due to oxygen 1.336, we may find the formula of the compound. If we remember that carbon is measured in units of 12 and oxygen in units of 16, then

$$0.500 \div 12 = 0.0416,$$

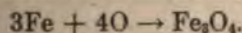
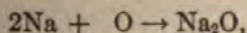
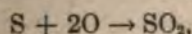
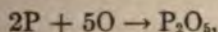
$$1.336 \div 16 = 0.0835.$$

The ratio  $0.0416/0.0835$  equals  $\frac{1}{2}$ , that is, for every unit quantity of carbon there are twice as many units of oxygen, and the formula of the compound therefore is  $\text{CO}_2$ . The equation representing the reaction may be written, since we know both sides of it, thus:



In any given experiment it is found that the ratio of chemical units is not expressed by whole numbers, but experience has shown that with increasing care in making experiments, thus eliminating errors, the mean of several results approaches integral values as a limit. Indeed, even with not very accurate work, by using large numbers of results, and thus compensating the errors made, by the so-called "law of averages" we get values remarkably close to integral. Thus the mean value of the relation for lead chloride from 75 results obtained by freshmen in the author's laboratory was 74.49 per cent lead, and consequently the formula is shown to be almost exactly  $\text{PbCl}_2$ , and similarly the mean of 41 results, also from freshmen, gave the value for potassium chlorate  $\text{KClO}_{3.012}$ .

In a similar, though not always so simple, manner we may determine the formulæ of other products mentioned to be  $\text{P}_2\text{O}_5$ ,  $\text{SO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{Fe}_3\text{O}_4$ , etc., and the corresponding reactions may be written:



**Rate of Reaction and Influence of Temperature.** — Attention has been called to the fact that iron, wood, etc., unite with oxygen slowly at ordinary temperatures. This process is called oxidation to distinguish it from the more rapid union with oxygen, which is called combustion or burning. Practically the distinction is that when oxidation is so rapid that the heat produced is great enough to cause some portion of the substances uniting, or of some of the products, to be heated to incandescence, it is called **combustion**. Later we shall see that the term oxidation is used with a broader meaning and that this present use is sometimes spoken of as oxidation in the narrower sense.

It will be observed that in all of the cases cited it was necessary to heat the substance in order to induce rapid union, *i.e.*, combustion. If careful attention is paid to this point we find that combustion begins at a much lower temperature with some substances than with others. This difference of "kindling point" is well illustrated by the lighting of the furnace fire. We raise the phosphorus on the head of a match to its kindling temperature by means of friction, on whatever surface is convenient, and its combustion produces sufficient heat to ignite, *i.e.*, raise to the kindling point, the match head and stick and this in turn, the paper in the grate. The heat of the burning paper ignites the wood and the burning of the wood produces heat sufficient to ignite the coal, at least when the experiment is successful.

The explanation of this phenomenon is as follows: The speed of reaction between oxygen and the elements with which it unites is a function of the temperature at which it takes place. In general the rate of chemical reaction is increased by rise of temperature. While the rate of increase varies somewhat in individual actions, an approximate statement is that the rate is doubled for each rise of  $10^{\circ}$  C. All the reactions given on pp. 36, 37 are exothermic (see p. 42) and may be assumed to be taking place at all temperatures, though in most cases at room temperature the rate is immeasurably slow. As the temperature is increased the rate increases and when a temperature is reached at which the heat evolved by the reaction is produced more rapidly than it escapes by radiation, conduction and convection (see the dictionary) the needed temperature for rapid action is maintained, and the action goes on spontaneously so long as new material and oxygen are both available. The temperature at which combustion is self-sustaining is known as the kindling temperature.



**Energy Relations.** — In our discussion of chemical changes we have confined our attention, so far as possible, to weight relations. Other considerations have, however, forced themselves on our attention. We will now consider these in more detail.

When iron and sulfur are heated together until rapid union begins, the process continues of its own accord even after external heating is stopped. The production of light and heat accompanies the conversion of iron and sulfur to iron sulfide. The same phenomena are observed to accompany the oxidation or combustion reactions described in the present chapter. On the other hand, the decomposition of potassium nitrate or of manganese dioxide ceases as soon as the required temperature is not maintained by external means. It appears, therefore, that heat may either be produced by chemical change or be absorbed by chemical change. In the decomposition of copper sulfate by means of the electric current, electrical energy is utilized (*vide* p. 6). If we place a stick of zinc and one of carbon in a solution of sulfuric acid and connect their external ends through an apparatus for measuring electric currents, we find electricity is produced while at the same time zinc is converted into zinc sulfate. Similarly, we might cite examples of the production of chemical change by means of light, *e.g.*, photographic processes, and we have noted the production of light by chemical change. Again, motion may be produced by chemical change, *e.g.*, the decomposition of explosives, and we may, by means of motion, *e.g.*, by rubbing mercury and sulfur together, produce chemical change. These examples illustrate the fact that chemical changes may either produce or consume heat, light, motion or electricity, *i.e.*, energy. Energy is defined by Ostwald as **work or anything which can do work or be converted into work**. While this definition is, perhaps, open to criticism it will be sufficient for our present purpose. Due to the labors of Lavoisier, Count Rumford, Joule, Helmholtz, Mayer and others, it has been shown that **the various forms of energy are mutually convertible without loss** (given perfect machines). This is known as the law of **conservation of energy**. Since, as we have seen, the various forms of energy are produced or consumed during chemical change we recognize chemical energy as one of the various forms. A convenient illustration of energy transformation is furnished by the following arrangement. A hot air engine is geared with a small dynamo and this in turn to a small electric lamp (Fig. 10). The engine may be set in motion by means of a Bunsen burner. We may note the following



transformations. The chemical energy\* of the gas is converted to heat, the heat to motion, motion to electricity, electricity to light. The transformations are not quantitative due to the character of the machines employed.

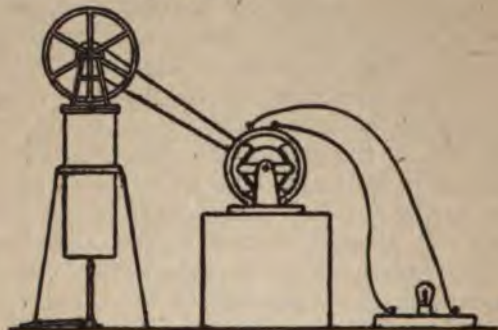


FIG. 10.

Heat is the usual form in which energy is liberated during chemical reactions, and hence the term **exothermic** ( $\epsilon\chi\omega$  = out and  $\theta\epsilon\rho\mu\eta$  = heat) is applied to reactions where heat or other form of energy is produced at the expense of chemical energy; and **endothermic** ( $\epsilon\nu\delta\omicron\nu$  = inner and  $\theta\epsilon\rho\mu\eta$  = heat) to reactions in which chemical energy is produced by the consumption of other forms. It ought to be observed that in those reactions where heat is given out the reaction frequently continues of its own accord if once started. This is a natural consequence of the effect of increase of temperature on the speed of reaction. (See p. 40.) On the other hand, endothermal reactions continue, as a rule, only when forced to do so by the use of energy from external sources. This difference is not peculiar to chemical changes alone, since in

\* The question will invariably arise in the mind of the student as to where the energy is which is liberated in the form of heat when, for example, carbon is burned. The answer can perhaps be best given in the form of analogy. If a weight is raised the energy absorbed can reappear in the form of motion or of heat when the weight falls. We say that the weight has potential energy by reason of its position and this energy becomes kinetic or active when it falls. Yet the raised weight possesses the energy only by reason of its relation to the earth, and a very different quantity of energy would be liberated if it fell, not to the earth, but to the moon. So carbon possesses a certain energy because of its relation to oxygen and energy exists in neither it nor the oxygen, but in their relation, and when carbon unites with chlorine a different amount of energy is liberated.

general it is true that physical changes also are spontaneous when they are accompanied by the liberation of some form of energy. There are many exceptions to the above statement, yet, as with rules in spelling, the generalization is valuable.

The importance of the energy changes which accompany chemical changes is very great. In these energy changes we find means of explaining chemical reactions and helpful suggestions for discovering new facts. Indeed, as a commercial factor energy is often of greater importance than mass. For example, we buy coal, not that by its combustion we may produce carbon dioxide, but that we may use the energy so obtained to minister to our comfort. We drink water largely, perhaps, because its capacity for heat absorption is very great, and hence much heat may be stored up with relatively small elevation of temperature. We use bread, potatoes, milk, etc., not for their mass value but for the sake of developing from them energy to replace that lost by muscular exertion, radiation, etc., in order to keep the human thermostat at  $98.6^{\circ}\text{F}$ . Clothes are worn, not alone for their beauty, but for their utility as conservators of the energy of the body.

**Quantities of Energy.**—In order to compare quantities of energy we must first establish a unit of measure. Two are in common use; the **calorie** and the **joule**. The **calorie** is defined as the quantity of heat required to raise one gram of water one degree centigrade. The **joule** is a quantity of energy equal to 0.238 calorie. (For further discussion of this relation see Chapter XXX and text books on Physics.) The relative heat capacity of substances is usually expressed in terms of **specific heat**. If, for example, the quantity of heat required to raise one gram of iron one degree centigrade is 0.1146 calories, the fact is ordinarily expressed; the specific heat of iron is 0.1146.

The quantities of energy involved in chemical change are usually expressed either in calories or joules and are determined by means of an instrument known as a calorimeter. One form of calorimeter is shown in Fig. 11. A sample determination may be described as follows: A gram of carbon is placed in an iron cylinder together with sufficient oxygen to combine with the carbon. The cylinder is placed in a vessel of water which is carefully insulated (*i.e.*, protected as nearly as possible from loss of heat). The combustion of the carbon is initiated by means of an electric current. The combustion of the carbon produces heat which raises the tem-



perature of the water. If now we take into account the specific heat of the iron cylinder, that of the calorimeter and the quantity of water, we may, from the rise of temperature, calculate the amount of heat produced by burning one gram of carbon. Careful

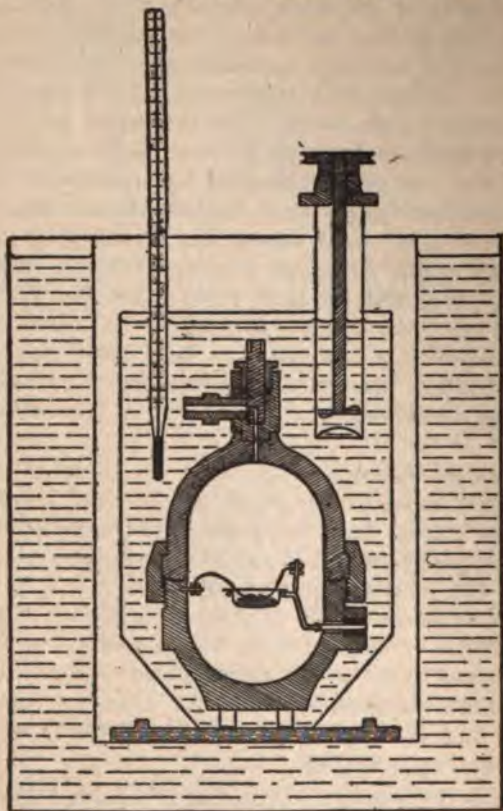


FIG. 11.

measurement of this quantity has shown it to be 8080 calories or 33,936 joules.

The heat produced by burning a gram of hydrogen is 34,179 cal. For one gram of sulfur it is 2250 cal. The heat produced for each **gram** of an element has not so much interest for chemists as that produced by unit chemical quantities. The usual form of expression is therefore the heat produced by a number of grams equal



to the atomic weight. These quantities are known as the **heat of combustion**. Frequently, also, the chemist is interested in the amount of heat, or other form of energy, concerned in relative chemical quantities of the products of combustion. This is the **quantity of energy involved in the production of a formula weight in grams of a given substance** and is known as the **heat of formation**.

In the table below are given the quantities of energy involved in the union of a few elements with oxygen.

Substance burned.	Substance formed.	Heat of combustion.		Heat of formation in calories.	Heat of formation in joules.
		Calories per gram.	Per gram atomic wt.		
Carbon.....	Carbon dioxide.....	8,080	96,960	96,960	408,232
Sulfur.....	Sulfur dioxide.....	2,250	72,135	72,135	302,400
Hydrogen....	Hydrogen oxide (water)	34,179	34,449	68,898	289,371
Phosphorus { (yellow) }	Phosphorus pentoxide.	5,966	184,950	369,900	1,553,580
Mercury.....	Mercuric oxide.....	105	21,000	21,000	88,200
Iron.....	Iron oxide ( $\text{Fe}_2\text{O}_3$ ).....	1,616	90,200	270,600	1,136,520

The following points are to be clearly recognized. A necessary consequence of the law of conservation of energy is that whatever quantity of energy is produced, or absorbed, when a compound is formed, exactly the same quantity is required to separate it again into its constituents. This is, of course, found to be the case, else we should not have the law. All of the compounds in the above list are exothermal. There are, however, many endothermal compounds and these, when decomposed, liberate energy, *e.g.*, hydrogen peroxide (see p. 92) on **decomposing** into water and oxygen liberates 23,100 calories of heat. We therefore frequently use the term **heat of decomposition**. While the heat of formation of carbon dioxide is 96,960 cal. and, therefore, its heat of decomposition to carbon and oxygen is - 96,960 cal., it must not be assumed that the simple presence of that quantity of energy is sufficient to effect this decomposition. It must be present in available form. Indeed, any **quantity** of heat at **temperatures** below 1000° C. is entirely without effect upon the composition of carbon dioxide. The suitable conditions for such absorptions of energy are various and will appear from time to time in subsequent discussion.

**Uses of Oxygen.**—Oxygen, as found in the air mixed with various other substances, enters into a large number of operations

directly and indirectly useful to man. Animals use oxygen in the process of respiration, both as a means of maintaining the body temperature and of removing worn out material. In plants, respiration is also one of the vital processes. The oxygen of the air, also, with the aid of bacteria, effects the decay of dead animals and plants, thus preventing accumulations of waste and making way for new life. In the sea, dissolved oxygen serves in the same general way the purposes of submarine life. Oxygen from the air takes



FIG. 12.

part in the processes of combustion, whereby energy is liberated and is utilized for manufacturing and other purposes. These operations are so familiar as not to need detailed mention. When in any of the processes mentioned special rapidity of action is desired, pure oxygen may be used instead of air. For such purposes oxygen is marketed in steel tanks (see Fig. 12). The gas pressure in these tanks is sometimes as high as 3000 pounds per square inch. This compressed oxygen is used in oxy-acetylene and oxy-hydrogen flames for welding and other high temperature operations. It is also used in conjunction with anæsthetics in surgical operations. Compressed oxygen, or oxygen manufactured as used from oxone and water (see p. 30), is also used in submarine boats

and caisson tunnelling to replenish the oxygen used up by the occupants of the boats or caissons. Also oxygen is used in pulmotors, or lung motors, for resuscitation of drowned or asphyxiated persons and for administration in critical illnesses.

**Compounds.**—In the introduction to this chapter attention was called to the very great number of elements with which oxygen unites. The substances produced by the union of oxygen with any one other element are known as **oxides**. These are distinguished from each other by adding to the term oxide the name of the other element; thus we may speak of the oxide of carbon, oxide of iron, etc. Frequently, also, the order is inverted and the preposition omitted; thus copper oxide, silver oxide, etc. When an element has more than one oxide, there are several methods of distinguishing between them. The method generally employed is to use the ending *ic* for the form which has the larger proportion of oxygen and the ending *ous* for the one containing a smaller proportion. As examples may be cited, cupric oxide ( $\text{CuO}$ ) and cuprous oxide



( $\text{Cu}_2\text{O}$ ); ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and ferrous oxide ( $\text{FeO}$ ). Sometimes this system does not suffice, as when there are several oxides of the same element or convention has established another usage. Thus, we usually employ the terms sulfur trioxide ( $\text{SO}_3$ ) and sulfur dioxide ( $\text{SO}_2$ ) though sulfuric oxide and sulfurous oxide would be also correct. Oxygen also forms compounds with two or more elements at the same time; such as sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ), alcohol ( $\text{C}_2\text{H}_5\text{O}$ ), potassium chlorate ( $\text{KClO}_3$ ), etc. The number of compounds is therefore very great. These may obviously be more satisfactorily discussed when we are familiar with the other elements concerned.

**Ozone.**—The discussion of oxygen is not complete without reference to a form of the element, known as ozone. This substance has a set of properties very different from that which describes oxygen. It is, however, prepared from oxygen by change of energy relations only, and the products of its reaction with other substances are the same as those produced with ordinary oxygen. This sort of relation is not uncommon among the elements and is known as *allotropy* (*vide* carbon, phosphorus, etc.) ( $\delta\alpha\lambda\lambda\omicron\varsigma$  = other and  $\tau\rho\acute{o}\tau\omicron\varsigma$  = form).

**Occurrence and History.**—When electrical discharges take place through air or oxygen a penetrating odor is produced. These discharges are such as those produced in the operation of frictional electrical machines or when bad connections are made in electrical operations where currents of high voltage are employed. The odor was first noted by Van Marum (1785) and by Schönbein (1840) was shown to be due to a distinct substance for which he proposed the name ozone ( $\acute{o}\zeta\alpha\nu$  = to smell). In 1860, Andrews showed that it could be produced from pure oxygen by electrical discharges and that its formation is accompanied by a contraction in volume. It is sometimes said to be present in the air, but its chemical properties (*q.v.*) are such as to render the statement somewhat doubtful (see *Sci. Am. Sup.* 79, 286).\* In any case, the "pure ozone" of the seaside and forest health resorts is a myth. It probably is present, temporarily, in the neighborhood of lightning discharges and it is, probably, the source of the superstition concerning the odor of Satanic apparitions which "disappear with a flash of lightning and an odor of sulfur."

\* See also, H. N. Holmes, *Am. Chem. Jour.*, Vol. 47, p. 497 (1912).



**Preparation.** — The most convenient method of preparing a small quantity of ozone is to allow phosphorus to oxidize slowly in the air. If this is done by placing a stick of yellow phosphorus in a beaker, partially covering the phosphorus with water and the beaker with a watch glass, the odor may be detected after a few minutes by removal of the cover. Larger quantities of the gas may be prepared by the so-called silent discharge through oxygen. This is most readily done in the apparatus indicated in Fig. 13. A stream of oxygen is passed through the space between the inner and outer tubes while at the same time a small Ruhmkorf coil actuated by a couple of storage cells is attached to the binding posts. Only a small fraction of the oxygen passing through the apparatus is converted to ozone. Ozone is also formed in small quantities at the anode when water is decomposed by electrical currents of high voltage. It is produced in larger quantities when fluorine decomposes water and when peroxides are treated with sulfuric acid.

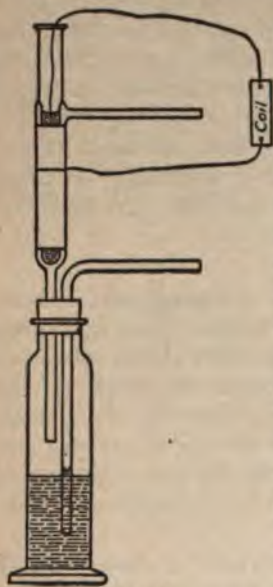
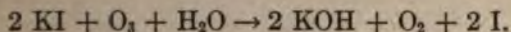


FIG. 13.

are treated with sulfuric acid.

**Properties and Uses.** — Ozone is a gas of marked and characteristic odor. Odors can only be described by comparing them with odors already known. If we say, then, that the odor of ozone is reminiscent of dilute chlorine and of sulfur dioxide we convey no information to one not acquainted with the latter substances. Ozone is more soluble in water than ordinary oxygen (50 vol. to 100 of water). Of course, when mixed with oxygen its solubility is proportional to its partial pressure. As already indicated, it is produced from oxygen and evidently by absorption of energy. Indeed, to produce 48 grams of ozone it is found that 32,400 cal. of energy are absorbed. It is, therefore, oxygen with a greater potential energy than the ordinary form. When ozone is produced from oxygen there is a decrease in volume from 3 to 2. This is also expressed by saying that its specific gravity, 1.658, is 1.5 times that of oxygen. As we shall see after certain theoretical considerations are presented, we may represent oxygen in its ordi-

nary form by the formula  $O_2$  and ozone by  $O_3$  (cf. Chapter V). Ozone differs chemically from ordinary oxygen in that it reacts more readily with those substances capable of oxidation and with a greater evolution of energy. It will oxidize certain elements at the ordinary temperature which are unaffected by oxygen, *e.g.*, silver and mercury. It will decompose certain compounds which are stable in ordinary oxygen and this fact accounts for its uses and also furnishes us means for its ready detection. For example, if paper moistened with a solution of potassium iodide (KI) is exposed to ozone the reaction indicated by the following equation occurs.



That is to say, potassium hydroxide (KOH), ordinary oxygen ( $O_2$ ), and iodine are formed. The formation of the free iodine is more readily indicated if starch is added to the solution in which the paper is soaked, since iodine produces with starch an intense blue color. The full meaning of the above equation will appear later.

Ozone has recently come into practical use for the purification of water (cf. p. 74), since when it is passed through water it destroys the bacteria which are the dangerous factors of polluted water. It may also be used for bleaching oils and for other purposes where oxidation at low temperatures is desired.

**Exercises.**—1. List in a tabular form reasons for beginning the detailed study of the elements with oxygen.

2. Calculate the percentage of oxygen in potassium chlorate,  $\text{KClO}_3$ ; glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ ; sand,  $\text{SiO}_2$ ; alcohol,  $\text{C}_2\text{H}_5\text{OH}$ ; nitroglycerine,  $\text{C}_3\text{H}_5(\text{NO}_3)_3$ .

3. Criticize the phlogistic hypothesis in the light of the now known facts concerning combustion. Why was it advanced?

4. Write the reactions involved in preparing oxygen from (a) water, (b) manganese dioxide, (c) potassium nitrate. Find how much of each substance must be used to get 10 liters of oxygen.

5. Determine the cost of oxygen per liter, so far as raw material is concerned, if mercuric oxide costs 20¢ per 100 grams; manganese dioxide, 2¢ per 100 grams; and potassium chlorate, 4¢ per 100 grams.

6. How many liters of oxygen gas are needed to make 1 l. of oxygen liquid (cf. sp. gr. of liquid with weight of 1 liter of the gas)?

7. Test your power of clear expression by stating the following laws differently from the text and yet correctly: Boyle's, Charles',



Henry's, Dalton's, Definite Proportions, Multiple Proportions, Combining Weights.

8. Distinguish between the terms, free oxygen, pure oxygen, and combined oxygen.

9. Give the names and formulas of four series of oxides illustrative of the law of multiple proportions. Tabulate these oxides, giving names and formulas, and show how in each case the law is illustrated.

10. Determine the formulas of the following compounds:

A. Per cent.	B. Per cent.	C. Per cent.
Ca..... 40.0,	C..... 39.78,	Na..... 22.77,
C..... 12.0,	H..... 6.97,	B..... 21.78,
O..... 48.0.	O..... 53.25.	O..... 55.45.

3.0 grams of carbon were burned to form an oxide weighing 11.0 grams; what is its formula?

11. Classify the oxides formed in the experiments on the chemical properties of oxygen under three heads (a) acid forming, (b) base forming, (c) insoluble.

12. If compounds show the following results upon analysis, what are their formulas?

A. Per cent.	B. Per cent.	C. Per cent.	D. Grams.
Hydrogen... 2.76,	Magnesium 25.53,	Iron.... 63.64,	Sulfur.... 36.48,
Chlorine... 97.23.	Chlorine... 74.47.	Sulfur.. 36.36.	Oxygen... 16.01.

13. Exercise clearness of expression by formulating in your own words definitions of (a) catalysis, (b) exothermic compound, (c) endothermic compound, (d) heat of formation.

14. 125 liters of air were collected over water at 20° and 745 mm. What volume of dry air at 0° and 760 mm. can be obtained from the moist air?

15. Given the following data concerning the volumes of gases collected over water, calculate in each case the volume of dry gas under standard conditions:

(a) Volume of gas, 100 c.c., temp. 20° C., barometric reading, 755 mm.

(b) Volume of gas, 200 c.c., temp. 3° C., barometric reading, 770 mm.

(c) Volume of gas, 200 c.c., temp. 65° F., barometric reading, 30 in.

16. Find what volume the sum of the above volumes would occupy at 20° C. and 740 mm.



17. How many calories of heat will it take to raise the temperature of 10 gms. of the following substances through  $10^{\circ}$ : (a) water, (b) iron (specific heat = 0.1146), (c) oxygen (specific heat = 0.15)?
18. If the heat produced by burning one gram of sulfur is 2250 cal., what is the heat of formation of sulfur dioxide? If the heat of formation of carbon dioxide is 96,960 cal., what is the caloric value of 1 gram of carbon?
19. Explain the more rapid combustion of phosphorus in pure oxygen as compared with air. Also explain why oxygen is used instead of air in a pulmotor.
20. If acetylene is endothermic, can you determine whether burning 10 grams of acetylene will bring about the liberation of more or less heat than burning the same relative quantities of hydrogen and carbon? The formula of acetylene is  $C_2H_2$ . In addition to the amount of heat liberated during combustion, what other factors determine the temperature reached?

## CHAPTER III

### HYDROGEN

**Occurrence.** — Reference to page 5 will call to the mind of the reader that hydrogen is number nine in the list of elements when considered from the standpoint of the relative quantity by weight. Since chemical values are measured in terms of atomic weights, we can determine the relative importance in chemical terms by dividing the values given in terms of weight by the atomic weights of the respective elements. Thus, we obtain the following order:

1. Oxygen.....	49.85 ÷ 16	= 3.11.
2. Hydrogen.....	0.97 ÷ 1.008	= 0.96.
3. Silicon.....	26.03 ÷ 28.4	= 0.92.
4. Aluminium.....	7.28 ÷ 27	= 0.27.
5. Sodium.....	2.33 ÷ 23	= 0.10.
6. Magnesium.....	2.11 ÷ 24.36	= 0.085.
7. Calcium.....	3.18 ÷ 40.1	= 0.08.
8. Iron.....	4.12 ÷ 56	= 0.07.
9. Potassium.....	2.33 ÷ 39	= 0.06.

Hydrogen occurs free on the earth in relatively small quantities, there being not more than one part of it in 100,000 parts of the atmosphere. Yet it is continually present in varying quantities in volcanic gas and is an important constituent of natural gas. It is also found free in small quantities in meteoric iron and in pockets in rock salt. It is also presumed to be a large factor in the atmosphere of the sun, its lines being prominent in the solar spectrum. (See spectrum analysis.)

Combined hydrogen is both widespread and abundant, the more important forms being as follows: Water consists of 88.82 per cent oxygen and 11.18 per cent hydrogen. Almost all organic compounds, both vegetable and animal, contain relatively large amounts of hydrogen, as the following list of formulas will illustrate:

Cane sugar.....	$C_{12}H_{22}O_{11}$ .	Marsh gas.....	$CH_4$ .
Starch.....	$(C_6H_{10}O_5)_x$ .	Chloroform.....	$CHCl_3$ .
Alcohol.....	$C_2H_5O$ .	Turpentine.....	$C_{10}H_{16}$ .



The element is an essential constituent of the group of substances known as acids. Of the acids the most common are hydrochloric (HCl), sulfuric ( $\text{H}_2\text{SO}_4$ ), nitric ( $\text{HNO}_3$ ), acetic ( $\text{HC}_2\text{H}_3\text{O}_2$ ), and hydrogen sulfide ( $\text{H}_2\text{S}$ ). Hydrogen is also an essential constituent of all bases of which sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) are the most common examples. Hydrogen also is a constituent of hydrates (see p. 82) and of many salts (see acid salts).

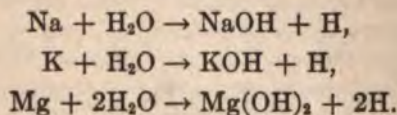
**History.** — Although both Basel Valentine (15th century) and Paracelsus (16th century) prepared hydrogen when they dissolved iron in sulfuric acid, neither made special mention of it. In the 17th century Boyle noted the inflammable character of this "air," but apparently this attracted little attention, since later chemists do not mention it. Lemery, in 1770, offered before the French academy, the explosion of hydrogen in air as a cause of thunder and also pointed out that it might be prepared from iron and hydrochloric acid. It was, however, confused with other combustible gases. It was Cavendish,\* an English scientist, who first, in 1766, recognized the element as a distinct kind of "air" or gas. He called it "inflammable air." He prepared the gas by treating various metals with hydrochloric acid and also with sulfuric acid. Priestley and Watt (of steam engine fame) apparently first observed that the combustion of "phlogiston," as they considered the gas, with "dephlogisticated air" (oxygen) produced water. In 1787, Cavendish published quantitative measurements showing the composition of water. Lavoisier claimed to have made this demonstration, but apparently he obtained information of Cavendish's experiments in advance of their publication, thus giving rise to the so-called "water controversy." (See Thorpe's Essays.) It is certain, however, that the first analysis of water was made by Lavoisier by decomposition of water by means of iron (see Mendeleeff, General Chemistry, p. 114). The name we owe to Lavoisier (from  $\text{ὕδωρ}$  = water and  $\gammaένειν$  = to produce).

**Preparation.** — 1. **Electrolysis.** Hydrogen may be readily prepared by the electrolysis of water in an apparatus similar to that shown in Fig. 5. Since pure water is not a conductor, the liquid used in the apparatus must be made to conduct by the intro-

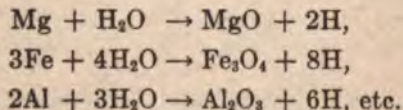
\* See Thorpe's Chemical Essays, Cavendish and Priestley.

duction of some substance such as sulfuric acid, sodium hydroxide, etc. A fuller explanation of the function of these dissolved substances will be given later (see Ionization Hypothesis). For the present we may content ourselves with the observation that the effect of the passage of the current is to separate the water into its constituents and when the operation is performed it is found that somewhat more than two volumes of hydrogen are produced, as compared with the one of oxygen. For an explanation of the excess hydrogen over the theoretical volume relation of 2 to 1, compare the solubility of hydrogen (*vide infra*) with that of oxygen and the mode of preparation of ozone (p. 48). This mode of preparation of hydrogen is used on a commercial scale, but shares the field with the decomposition of steam and of sulfuric acid by iron (*vide infra*).

**2. Metals and Water.**—Hydrogen may be prepared from water by reaction with metals. There is, however, very great variation in the rapidity of the action. Thus, at ordinary temperatures sodium and potassium react upon water with extreme vigor, the latter with such violence that the hydrogen is ignited from the heat of the reaction. Magnesium, finely powdered, acts more slowly. These metals do not free all the hydrogen, but produce a class of bodies called hydroxides. The reactions take place as indicated by the equations:



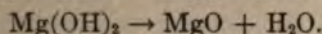
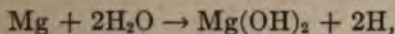
At elevated temperatures other metals also free hydrogen from water and form, not the hydroxide, but the oxide of the metals. If we pass steam over highly heated metals, such as iron, magnesium, zinc, etc., the following reactions take place:



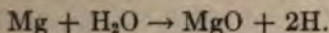
These reactions are not essentially different from the ones above given, since if we heat magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , or the corresponding hydroxides of other metals, they decompose,



forming the oxides. We may, therefore, look upon the latter reactions as being the final stage of two successive steps, *e.g.*,



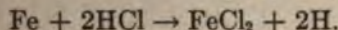
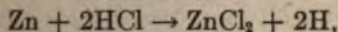
If we now add these two equations algebraically we get



This mode of consideration of successive chemical reactions will later receive fuller attention.

When the metals which decompose water are arranged in the order of the speed with which they react, the order is found to be that of the same metals in the electromotive series (see p. 390). They will also be found to precede hydrogen in the series. The other metals which follow hydrogen may be heated with steam, without any production of hydrogen. The same order of activity of metals will be noted in other connections. An explanation will be offered later (see p. 501). Since copper follows hydrogen in the electromotive series, it and its alloys, brass, bronze, etc., are frequently employed where cheaper metals would be undesirable, *e.g.*, in steam whistles.

**3. Metals and Acids.** — Hydrogen is most conveniently prepared by the treatment of certain metals with certain acids. For example, if zinc or iron be treated with a solution of hydrochloric acid, reactions represented by the following equations occur:



The hydrogen may be conveniently collected by displacement of water, using the apparatus illustrated in Fig. 14. Another type of apparatus may be used when the gas is needed in considerable quantity. This is known as Kipp's apparatus (Fig. 15). When the gas flow is stopped by closing the stop cock, the acid is automatically removed from contact with the metal and contact is again brought about when the gas is allowed to escape.

The following points regarding the action of acids with metals are to be noted. If an acid is placed upon a metal, action takes place only at the surface of contact. Since powdered metals offer a larger surface per unit weight than do the same metals when in compact form, the more finely divided a metal is, the more rapidly,



other things being equal, it reacts with an acid. Thus powdered zinc evolves hydrogen from an acid much more rapidly than does the granulated or stick form.

The same variation in speed of action of the different metals upon a given acid is to be observed as in the case of their reaction upon water. Thus sodium and potassium react with hydrochloric acid very rapidly, zinc and iron slowly, tin and lead very slowly, copper and mercury not at all (*cf.* Electromotive series, p. 390). In comparing the speed of reaction of different metals, it should be noted that since the action of acids upon metals is in all cases exothermic unless the initial speed is the same, the heat evolved will increase the rate of one reaction more than that of another.

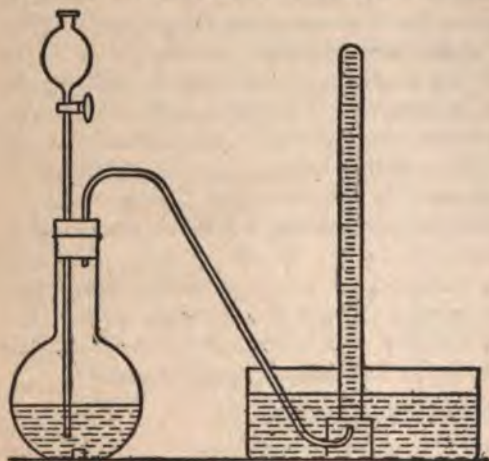


FIG. 14.



FIG. 15.

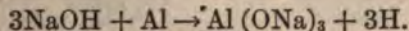
If a stick of zinc be placed in dilute acid and carefully observed, bubbles of hydrogen will be seen adhering to its surface. It is obvious that the presence of these bubbles interferes with the desired intimacy of contact between metal and acid. If, however, a stick of zinc and a platinum plate are immersed in acid, and the two are connected outside the liquid by means of a platinum or copper wire, we have the familiar device known as an electrical couple. In this case, the bubbles of hydrogen will be observed to come from the platinum surface, although the chemical reaction is wholly upon the zinc. The zinc surface is wholly exposed to the acid. To a degree the same condition obtains if both metals

are wholly immersed. Hence platinum, or other inactive metal, in contact with an active one increases the rate of action of the acid catalytically. In the same way, impurities in a metal, furnishing as they do many such couples, increase the rate of action between the metal and acid.

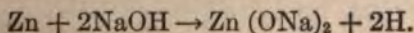
With respect to the acids used, there is also variation. If the rates of evolution of hydrogen be measured when we use pieces of zinc of like size with hydrochloric, sulfuric and acetic acids of like concentration, it will be found that the rates are not equal. An explanation of this variation of rate will be given in Chapter IX (*q.v.*). It is, therefore, obvious that there is choice to be made among acids if we seek the one most appropriate for the purpose. This becomes especially apparent when we find that if we treat active metals with nitric acid, no hydrogen is obtained although the metals are rapidly dissolved (*cf.* Chap. XVI). If zinc or other active metal is treated with concentrated sulfuric acid (*i.e.*, acid free from water), little or no evidence of chemical reaction at room temperature is observed. If the metal and acid are heated together, vigorous action occurs but no hydrogen is formed. On the other hand, if dilute sulfuric acid (*i.e.*, acid mixed with more or less water) be placed upon zinc, hydrogen is rapidly evolved. It can, however, be shown that the hydrogen does not come from the water. We may then say that the water acts as a catalytic agent. An explanation of its function is given in Chapter IX.

We may sum up the foregoing observations upon the preparation of hydrogen from acids by saying that **certain metals when treated with certain acids in solution liberate hydrogen at a rate depending upon the character of the metal and acid used, and upon the temperature and the catalytic agents present.**

**4. Metals and Bases.** If aluminium is allowed to stand in contact with a strong solution of sodium or potassium hydroxides, hydrogen will be slowly evolved and a substance called sodium aluminate will go into solution. The reaction is indicated by the equation,



In a similar manner several other metals liberate hydrogen from bases, either in solution or when the dry substances are heated together. An example is furnished by zinc, which, if heated with sodium hydroxide, reacts as indicated:





**Purification of Hydrogen.** — Hydrogen as prepared by any of the methods described is always mixed with some water vapor and

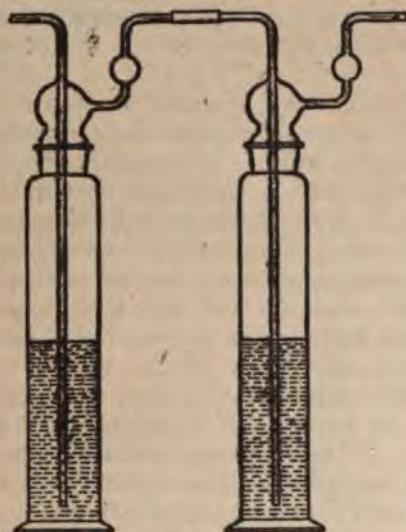


FIG. 16.

frequently with small quantities of other gases derived from impurities in the materials used. It is frequently desirable to remove these, and also any solid particles carried mechanically by the stream of gas. The impurities other than water can usually be removed by allowing the gas to bubble slowly through a gas washing bottle (Fig. 16) containing a solution of some good oxidizing agent such as an acidified solution of potassium permanganate. Water vapor may be removed by passing the gas through concentrated sulfuric acid. A plug of cotton wool placed at any point in the gas stream

will retain the solid particles. If the last traces of moisture are to be removed the gas is passed through a drying train, as shown in

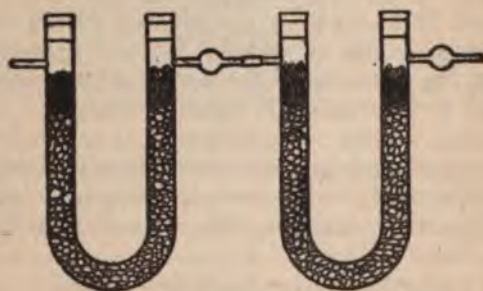


FIG. 17.

Fig. 17. The U tubes are filled with substances which absorb moisture readily, such as calcium chloride. The most efficient drying agent is phosphorus pentoxide.



**Physical Properties.** — It will be convenient to place the physical properties of hydrogen in tabular form and follow the table with discussion of certain of them.

Gas at room temperature.	Solubility in water, 2 vol. : 100.
Colorless.	Solubility in palladium, 501 vol. : 1.
Odorless.	Critical temperature, $-234^{\circ}\text{C}$ .
Tasteless.	Critical pressure, 20 atmospheres.
Specific gravity, 0.0695.	Specific gravity of liquid, 0.07.
Density ( $H = 1$ ), 1.	Specific heat (gas), 3.4.
Weight of 1 liter, 0.08987 g.	Boiling point (58 mm.), $-260^{\circ}\text{C}$ .

**Gas.** — The term gas as used in science is not susceptible of exact definition except in terms of the kinetic molecular hypothesis (see Chap. V). The term was apparently invented by Van Helmont, an alchemist (died 1644), to distinguish substances such as hydrogen from vapors which arise from hot liquids and condense again on cooling. The derivation of the word is unknown. We may say that a gas is a substance which expands automatically without limit unless confined and which fills any vessel in which it is confined.

**Density.** — The density of substances may be defined as the weight of unit volumes. Very frequently we desire to express the relative densities. For this purpose various modes of expression are in use. One frequently employed for gases is to state the weight in grams per liter when the gases are measured under standard conditions. Thus we say the weight of one liter of hydrogen is 0.090 grams; that one liter of oxygen is 1.429 grams; of air, 1.293 grams. Another standard method of comparison is in terms of **specific gravity**. Air is taken as the unit for gases (water as the unit for liquids and solids). Thus we find the relative weight of hydrogen compared with that of air under like conditions is as 0.0695 to 1. That is, the specific gravity of hydrogen is 0.0695. No other gas is so light as is hydrogen. It is, therefore, sometimes used as a basis for comparison. We ordinarily use the term density ( $H = 1$ ) to describe this relation. Thus the density of oxygen ( $H = 1$ ) is 15.96; that of air ( $H = 1$ ) is 14.4.

According to the principle of Archimedes (see Physics) any body supported in a fluid (gas or liquid) is buoyed up to an extent measured by the weight of fluid displaced. Since hydrogen is lighter than air, an enclosed volume of it tends to rise and this tendency may be utilized for the purpose of lifting other bodies.

The lifting power of hydrogen is, therefore, measured by the difference between the weight of hydrogen used and that of the volume of air displaced. For a liter of hydrogen at standard conditions in air under the same conditions the lifting power is therefore 1.203 grams. This property of hydrogen is utilized in many ways (see Uses). It is also because of the low density of hydrogen that it may be collected by downward displacement of air, and may be poured **upward** from one vessel to another (Fig. 18).

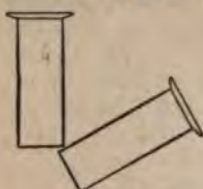


FIG. 18.

ment of air, and may be poured **upward** from one vessel to another (Fig. 18).



FIG. 19.

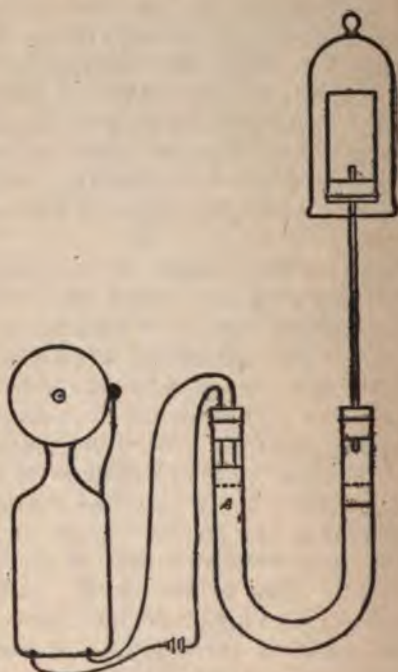


FIG. 20.

**Diffusion.** — When a vessel containing any gas is opened, the gas expands until it eventually fills all accessible space. This property of gases is called diffusion (*diffusus*, p.p. of *diffundere* = to spread). It may be illustrated by bringing the mouth of a cylinder containing ammonia over the mouth of a similar cylinder



containing hydrochloric acid gas. The progress of the diffusion may be traced by the white cloud formed when the particles of the two gases meet. Again, if we open a bottle of pungent perfume, the escaping gas will permeate a whole room. This power of auto-locomotion is common to all gases but the rate is a function of the density. The rate of diffusion of different gases was first studied carefully by Graham, a Scotch chemist (1838), and the following law determined. The rate of diffusion of gases is approximately inversely proportional to the square root of their specific gravities (or densities). Hydrogen, being the lightest gas known, moves most rapidly. The relative rates of motion of air and hydrogen ( $1 : \sqrt{0.0695} = 3.7 : 1$ ) may be beautifully illustrated by a sort of obstacle race. A quantity of air is confined in a porous cup fitted to a Woulff bottle as shown in Fig. 19. The Woulff bottle is partially filled with water, and fitted with an outlet tube as shown. A bell jar filled with hydrogen is lowered over the porous cup. Since hydrogen diffuses into the cup more rapidly than air finds its way out into the bell jar, the gas pressure within the cup increases and water is forced out of the Woulff bottle producing a fountain as shown in the figure. When the bell jar is removed, hydrogen then escapes from the cup more rapidly than air enters, thus creating a diminished pressure within the cup, and air is consequently drawn in through the jet tube. A similar illustration is shown in Fig. 20. Here the difference in rate is made to produce a rise of mercury in the limb A of a U tube thus completing the circuit of an electric bell attachment.

**Solubility in Water and in Solids.**—Hydrogen is even less soluble in water than is oxygen and hence may be collected over water with negligible loss. If, however, it is passed over warmed and finely divided palladium it is absorbed to a remarkable extent. This phenomenon was first observed by Graham\* and named occlusion (occludo = to shut up). The same phenomenon is also observed with other solids, thus, charcoal after ignition will absorb twice its volume of hydrogen; lead, 0.15; aluminium, 2.7; copper, 4.5; nickel, 17; iron, 19; platinum, 49; palladium, 501. The last named under special conditions will absorb nearly 900 volumes. Other gases are also occluded by solids, but not in the same ratios as with hydrogen. Thus molten silver occludes oxygen to a considerable extent, but does not occlude hydrogen at all. Ammonia is occluded to a very great extent by charcoal. This

\* Phil. Mag. 4, XXXII, p. 516.



absorption of gases by solids differs from the solution of gases by liquids in many particulars, but notably in that the solids



FIG. 21.

dissolve gases to a greater extent when hot. Also, possibly by reason of concentration in the metal, the chemical activity of occluded gases is materially increased. This is used to advantage in automatic gas lighters and in matchless cigar lighters. In these, finely divided metal, platinum or palladium, is, when saturated with oxygen from the air, exposed to an atmosphere of gas or wood alcohol and the reaction in the pores of the metal raises the temperature sufficiently to ignite the external materials. This method of starting combustion was discovered by Döbereiner, who devised a so-called lamp, shown in Fig. 21, in which platinized asbestos and hydrogen are used together with air. Whether the occlusion of gas

by a solid is a chemical reaction or not is a mooted question, the discussion of which in our present state of knowledge is fruitless.

**Chemical Properties.**— 1. **Direct Union with Elements.**

Hydrogen burns readily in the air. The flame produces so little light, as compared with an ordinary gaslight, that it is ordinarily called "non-luminous" or "colorless." As a matter of fact, the flame is somewhat luminous and is of a bluish tint. To illustrate this fact, the hydrogen should be burned from a jet equipped with a platinum or other non-volatile tip; otherwise the heat of combustion may volatilize the material of which the tip is composed giving color to the flame. With an ordinary glass tip, the color is an intense yellow. The color is due to the presence of sodium in the glass (see Flame Colorations, p. 421).

The heat of combustion of hydrogen is very great, 34,000 cal. per gram. If by means of a blast lamp (Fig. 22) the combustion of hydrogen is made very rapid, a very high temperature is produced. A blast lamp is so constructed that an intimate mixture of air or of oxygen and the gas to be burned is secured at the place of ignition. The temperature of the oxy-hydrogen flame in a

blast lamp is about  $2500^{\circ}\text{C}$ . This temperature is sufficiently high to melt platinum and many other refractory materials. It is also sufficient where the flame is directed against a piece of quicklime to heat the latter to an intense white heat. This method of obtaining an intense light was formerly much used in lantern projection and stage illumination, until displaced by the electric light. The light was variously known as the Drummond light (from the name of its inventor), as the calcium or limelight (from the material used) and as the spotlight (from the use made

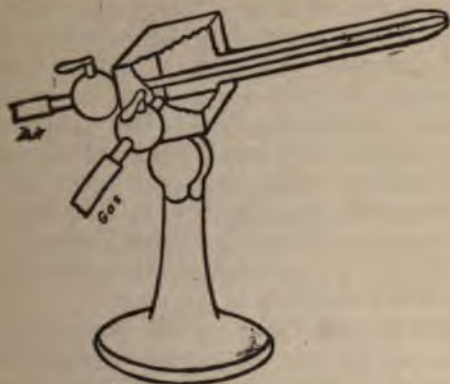


FIG. 22.

of it). The latter terms are used at present in various connections both figurative and literal.

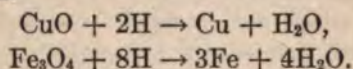
If hydrogen is mixed with air or with oxygen and then ignited, combustion takes place with extreme rapidity. The heat produced raises the temperature of the water vapor or of residual gas and there may be consequent sudden expansion of volume, *i.e.*, an explosion. This is well illustrated by the laboratory toy known as the "hydrogen gun." It may also be shown by blowing soap bubbles by means of a mixture of oxygen and hydrogen. The bubbles when ignited explode with surprising violence. When hydrogen issuing from a jet is ignited, some intermingling with the air has always taken place so that the ignition is accompanied by a miniature explosion known as the "characteristic pop" of hydrogen. A mixture of hydrogen and oxygen does not react apparently at ordinary temperature. When a mixture is kept at  $300^{\circ}$ , several days are required for complete combustion. At  $518^{\circ}$  the union is complete in a few hours. At  $600^{\circ}$  the union is



rapid but not explosive. At 700° it is so rapid that we say it is of explosive violence. It is probable that even at room temperature the reaction goes on but at a rate not susceptible of measurement. It is estimated that many million years would elapse before measurable progress of the reaction would be made.

Hydrogen unites with fewer elements than does oxygen. It is also as a rule much less active at ordinary temperature. Fluorine is the only element with which it reacts rapidly at room temperatures (15° to 20°). With chlorine the reaction is slow at room temperature but the rate is vastly increased by increase of temperature, by the presence of catalytic agents and particularly by sunlight (*cf.* Chlorine, Chapter VI). When hydrogen has combined with fluorine, chlorine, bromine or iodine, the products, if dissolved in water, are strong acids. The compounds with sulfur, selenium and tellurium are weak acids. Hydrogen unites with certain metals forming compounds which may be re-crystallized from liquid ammonia (see Potassium, Chapter XXIII). The compounds of hydrogen with other single elements might properly be termed hydrides. As a matter of fact, the term is only used when speaking of the hydrides of the metals.

**2. Reduction by Hydrogen.**— We have seen (p. 29) that oxides and other oxygen compounds when heated show a tendency toward decomposition with liberation of oxygen. This tendency is favored by the presence of hydrogen. If copper oxide, iron oxide, etc., are heated in a stream of hydrogen, the oxides are converted into metals and water is produced as indicated in the following equations.



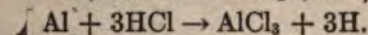
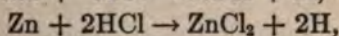
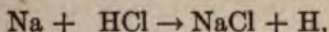
Processes such as these are called reductions. It will be seen that in the cases cited the oxide is reduced while hydrogen is oxidized. Indeed, in the widest sense the two processes are inseparable and the oxidation of one substance is coincident with the reduction of another (*cf.* p. 228).

All oxides are not reduced by hydrogen at temperatures readily obtained. Thus laboratory experiments will show the student that at the temperature obtained by the Bunsen burner, aluminium oxide,  $\text{Al}_2\text{O}_3$ , is not reduced by hydrogen. The stability of the oxides of metals towards reduction is in inverse order to the position of the metals in the electromotive series (p. 390). Oxides

of the metals above aluminium are not reduced at available temperatures while those below are, and indeed the more readily, the lower the metal in the series.

A very interesting class of reducing actions is furnished by hydrogen when it is just being liberated from compounds. We can remove easily oxidizable materials from hydrogen by passing the impure gas through acidified potassium permanganate with but very little oxidation of the hydrogen. If, however, we liberate the hydrogen in the permanganate solution by addition of a little zinc the effect of the presence of the metal is very greatly to facilitate the oxidation of the gas. This is a typical case of increased activity of elements when they are in the act of being liberated and was for a time supposed to be due to a special state of the element, known as the "nascent state." The fact that the rate of action depends upon the metal used has led to the assumption that it is due to what is known as "contact action" in which the metal is said to act "catalytically." In most cases the increase of speed is probably due to the increase of concentration of the reacting element, the increased concentration being due to occlusion.

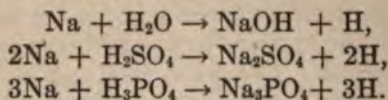
**Valence.** — If we write the equations representing the quantity of hydrogen liberated from hydrochloric acid by one atomic weight of sodium, one of zinc and one of aluminium, we get the following:



It is apparent that the atomic weights of these three elements differ not only in the amount of hydrogen displaced but in the quantities of chlorine held in combination. If we examine the other equations in this and the two previous chapters, we shall note similar relations. Thus, one atomic weight of sodium displaces one of hydrogen from water and one of magnesium displaces two. This property of the atomic weights of the elements is termed **valence**. If we consider the valence of hydrogen as unity, we may express that of another element in terms of hydrogen. Thus an atomic weight of sodium in the above equation has the same valence (combining value) as hydrogen. We speak of it therefore as univalent. Zinc is bivalent and aluminium is trivalent. We may also use Greek instead of Latin numerals. Thus sodium, zinc and aluminium are mono-, di- and trivalent respectively.



Also, in considering the equations of this chapter, we may note that certain portions of compounds consisting of more than one element appear to be transferred from one compound to another intact. These groups we will call radicals. Thus we find the group  $\text{SO}_4$ , called the sulfate radical, in copper sulfate,  $\text{CuSO}_4$ , zinc sulfate,  $\text{ZnSO}_4$ , aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , sulfuric acid,  $\text{H}_2\text{SO}_4$ , etc. These radicals have each a distinct valence. This may be illustrated by the following equations:



The radicals,  $\text{OH}$ ,  $\text{SO}_4$  and  $\text{PO}_4$  are respectively mono-, di- and tri-valent.

Valence may now be defined as **the numerical combining value of atomic weights of the elements and formula weights of radicals in terms of hydrogen as unity.**

It is usually possible to ascertain the valence of an element by an inspection of the formulas of its binary compounds (*i.e.*, compounds with one other element) provided we know the valence of the other element. Thus, since hydrogen is the unit of valence, chlorine in hydrochloric acid,  $\text{HCl}$ , is univalent. Since the formula of water is  $\text{H}_2\text{O}$ , oxygen may be regarded as bivalent. With these starting points then,  $\text{AlCl}_3$  and  $\text{Al}_2\text{O}_3$  indicate for aluminium a valence of three,  $\text{Fe}_2\text{O}_3$  and  $\text{FeCl}_3$  a valence for iron of three. With compounds of more than two elements, it is not possible to ascertain valence relations by inspection except where we consider them made up of a radical with one other element. Thus, if we consider potassium permanganate,  $\text{KMnO}_4$ , as made up of the element  $\text{K}$  and the radical  $\text{MnO}_4$ , we may expect the radical  $\text{MnO}_4$  to be univalent since potassium is univalent. The student is urged to note the valence of the elements and radicals as they come under his observation, as this knowledge is of great assistance in learning the exact composition of compounds as expressed by formulas.

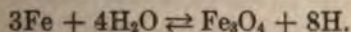
Too much confidence is not to be placed in the method of learning valency by inspection. Thus the formulas  $\text{Fe}_3\text{O}_4$  and  $\text{H}_2\text{O}_2$  give no clue to the valency of either iron or oxygen. Further, it is to be observed that many elements have variable valency. If the above discussion leaves a feeling of uncertainty and dissatisfaction in the mind of the student, he is asked to be patient and use the conception of valence as a tool. The full and satisfactory explana-

tion must await the knowledge of certain facts and hypotheses not yet at hand. These will be found in subsequent chapters (cf. p. 100).

**Affinity and Reversible Changes.** — It will have been observed that oxygen unites readily with hydrogen and with many other elements. Hydrogen unites with fewer elements and as a rule less vigorously. In order to account for these and similar facts, we assume the existence of a certain attractive force which is the cause of chemical union. This attractive force we call **chemical affinity**. What it is, we simply do not know. In this respect it is on the same plane as gravitation, love and sundry other causes of action. While we do not know what chemical affinity is, yet, if we assume the existence of such a force, we can ascertain the manner and extent of its operations and the laws which govern them and thus achieve one of the objects of chemical study: a control over the processes of nature. We note then that the existence of an attractive force between elements is assumed as a necessary antecedent to chemical reaction, and upon the intensity of this force depends the rate of combination of elements under given conditions and upon which the stability of the compounds produced also depends.

The assumption of chemical affinity as a cause of chemical reaction is not alone a sufficient explanation of all the reactions discussed in this chapter. For example, we observe that hydrogen and an iron oxide are produced when steam is passed over heated iron (p. 54) while when a stream of hydrogen is passed over heated iron oxide, water and iron are produced. The reaction evidently goes either way according to the conditions.

This situation is not unique and reactions of this type are called **reversible reactions**. Reversible reactions may be indicated by use of the double arrow symbol  $\rightleftharpoons$ . Thus:



That affinity alone does not account for such reactions is clear. If we assume in the above case that iron decomposes water because it has a greater affinity for oxygen than hydrogen has, we are by the reverse reaction led to the absurd conclusion that hydrogen reduces iron oxide because it has a greater affinity for oxygen than has iron. As a matter of fact, we note that water is decomposed by iron when a given set of conditions is met and the reverse



reaction takes place when a different set of conditions is provided. We may say, then, that the character of chemical reaction depends upon the affinities of the reacting materials and upon the conditions of reaction. The laws governing reversible reactions will be summarized in Chapter VII.

**Uses.** — Hydrogen finds many practical uses. It is a component of natural gas and of nearly all artificial fuel gases, such as coal gas (p. 348) and water gas (p. 348). It is therefore used as a fuel. It is used by the braziers and jewelers in the oxy-hydrogen blow-pipe for providing high temperatures. It is also used in the manufacture of ammonia (see p. 264). Its most conspicuous application is for the inflation of balloons. These range in size and importance from the toy balloons sold on the street corners and at county fairs to the huge war balloons of the Zeppelin type. The latter attained special importance in the World War and it is of interest to note their vast size. The war Zeppelins are from 150 to 160 meters in length; 14 to 17 meters in diameter and hold from 22,000 to 30,000 cubic meters of gas. Their carrying capacity is therefore very great and their destructive possibilities enormous. It is also of interest to observe that the hydrogen for filling them is prepared by electrolyzing solutions of common salt. The other products of the electrolysis are sodium hydroxide and chlorine (cf. Chlorine Uses, p. 122).

**Compounds.** — The compounds of hydrogen are both numerous and of vast importance, since it enters into the composition of such substances as petroleum, wood, starch, muscle and brain tissue, etc. It is also an essential constituent of acids and bases and hence it is important in inorganic chemistry. Perhaps its most important compounds are with oxygen, *viz.*, water and hydrogen peroxide. These are so valuable and indeed fundamental in the inorganic chemical system that a special chapter will be devoted to them and in every other chapter the chemistry of water will unavoidably play a part. The study of other hydrogen compounds is taken up with that of the other elements with which it combines.

**Exercises.** — 1. Calculate the percentage by weight of hydrogen in marsh gas,  $\text{CH}_4$ ; alcohol,  $\text{C}_2\text{H}_6\text{O}$ ; turpentine,  $\text{C}_{10}\text{H}_{16}$ .

2. Assume that all the hydrogen can be readily isolated fr

each of the three compounds in Exercise 1 and calculate the volume to be obtained under standard conditions from 10 grams of each.

3. Write the equations for the reactions between sodium, potassium, and magnesium, and cold water, and determine how many grams of each metal are needed to procure 22.4 liters of hydrogen under standard conditions. Compare the weights found with the atomic weights of the metals.

4. The heat of the reaction  $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + 2\text{H}$  is 34,400 calories when the reaction is carried out in a solution in water. How much increase of temperature will take place when 6.5 grams of zinc are dissolved in 500 cubic centimeters of the dilute acid, assuming no loss by radiation or otherwise? Assume also the solution to weigh 500 grams and to have unit specific heat.

5. Calculate the volume of a hydrogen balloon needed to just balance a weight of 100 pounds; assuming standard temperature and pressure conditions.

6. Make a list of all the equations given in Chapters I, II and III and classify the elements or radicals involved in the changes according to the valence shown.

7. What are the radicals of: Phosphoric acid, sulfuric acid, nitric acid, hydrogen sulfide, sulfurous acid, sodium nitrate, potassium carbonate, hydrofluoric acid, hydrofluosilicic acid? Indicate the valence of each radical. (Use index to obtain formulas.)

8. (a) What are the formulas for the aluminium salts of sulfuric, nitric, tartaric, phosphoric, and hydrochloric acids?

(b) What are the formulas for calcium fluoride, sodium carbide, lithium hydride, lithium nitride, chlorine dioxide?

9. Give the formulas for ferrous oxide, ferric oxide, chromous chloride, chromic chloride, manganous and manganic hydroxides.



## CHAPTER IV

### WATER

**Occurrence.** — It has been estimated by LeConte that if the earth were perfectly smooth and round, enough water is found on the earth to cover it uniformly to a depth of more than two miles. It actually does cover three-fourths of the surface to a varying depth. It is found in three states of aggregation: as vapor in the air, as liquid in and on the surface of the earth, and as a solid, ice and snow. Also, many substances which appear to be dry will on heating give abundant quantities of water. For example, the human body yields on desiccation about 66 per cent water, land plants 50 per cent to 75 per cent and even clay about 14 per cent.

When water in the liquid condition is given free opportunity to do so, it tends continuously to change into the gaseous form, water vapor, at a rate which is a function of the temperature. Heat is absorbed in the process. Thus, air above water surfaces receives a certain amount of vapor which is carried along with the air currents, and by its own tendency to expand indefinitely, to a place more or less remote from the water surface. When the vapor reaches regions of lowered temperature, a part of it may be condensed to liquid or solid form and produce clouds, fog, dew, rain, frost or snow. This process liberates heat. The heat liberated by condensation of water vapor has enormous effect on climatic conditions. As the rain falls through the air, it takes up a certain quantity of materials from the air, dust particles and gases, so that even as it falls it is more or less "impure." When it reaches the surface, it comes in contact with various substances capable, to varying degrees, of uniting with the water to form a homogeneous liquid, called a solution. How much material is so dissolved varies, of course, with the local conditions, but so far as we know, there is always some material dissolved. Pure water is, therefore, unknown in nature.

If rain water is collected on clean and practically insoluble surfaces it contains a very small amount of solid matter, *i.e.*, matter which remains behind on evaporation of the water, seldom more and usually less than 3.5 parts per million, but it contains approxi-

ly 0.013% nitrogen, 0.0064% oxygen and 0.0013% carbon dioxide. On reaching the surface of the earth, some of the water is immediately vaporized by heat from warm surfaces, some runs along the surfaces and some sinks down into the earth to reappear in part at lower levels as springs. The content of the surface water, of course, varies as the materials vary with which it comes in contact; but such water is potable, if it does not carry along in suspension unusual amounts of clay and other easily transported materials, which settle out on standing — sediment. If it does carry large amounts of such material in suspension or if it has been in contact with matters offensive to sight or taste it is said to be non-potable, *i.e.*, undrinkable. Surface water may, however, be "potable," and still be unsanitary. It may come in contact with human or animal refuse or with poisonous material and so carry disease germs or poisonous substances. Whether surface water is fit for human consumption is a question which ought to be decided by analysis, chemical and bacteriological.

The portion of water sinking into the earth ultimately seeks the surface in the form of springs, except such portions as have slowly evaporated from the surface. The spring water, of course, joins the streams and so becomes "surface water" again. The spring water may reach only very insoluble rocks and hence appear with a mineral content but slightly different from the surface water. Usually, however, it dissolves some rock material such as limestone or gypsum and reappears as "hard water," *i.e.*, water which feels harsh to the touch and which destroys the lather making tendencies of soap and water by destroying the soap. Or the water may come in contact with materials such as sodium carbonate or sodium sulfate and so have a bitter taste and a tendency to froth when agitated. Such water is known as alkaline water. If in special cases a source of water contains an unusual quantity of some dissolved material or materials, the water is known as mineral water and the spring as a mineral spring. The actual amount of material dissolved in mineral water need not be large. It is essential only that it be, or be considered, unusual. Mineral waters are frequently highly valued for some real or fancied medicinal value of the dissolved substances. They are variously named from their location or some special constituent. The most important classes from the latter viewpoint are:

- Chalybeate water . . . . . containing ferrous carbonate.
- Sulfur water . . . . . containing hydrogen sulfide.
- Carbonated water . . . . . containing carbon dioxide (usually under pressure).
- Saline water . . . . . containing epsom salts ( $\text{MgSO}_4$ ); sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), or other material having a laxative effect.
- Lithia water . . . . . containing lithium carbonate or chloride.



If a spring issues from the earth, both hot and mineralized, it is especially prized. Some of the most famous health resorts depend upon the mineral spring as the fundamental factor, but it is quite probable that most of the beneficial effects of the so-called "cures" are due to a combination of faith, change of habits, and special medical attention quite as much or more than to the, in many cases, undoubted physiological effects of the waters. In any case, mineral waters can be, and frequently are, manufactured in exact imitation of the natural product.

Eventually all rain water, not evaporated, finds its way with its burden of dissolved materials into the sea, which is the great septic tank of nature. Here dissolved organic materials decay and the mineral matters accumulate. To follow the matter further is the province of the geologist. The sea water contains about 3.6 per cent dissolved material, of which the largest factor is common salt.

The following may be considered as a representative analysis of the mineral content of sea water.

Pacific Ocean.	Parts per 1000.
Fixed residue.....	34.700
Sodium.....	10.262
Chlorine.....	18.950
Magnesium.....	1.3151
Calcium.....	0.4719
Potassium.....	0.6038
Sulfate ( $\text{SO}_4$ ).....	2.786
Bromine.....	0.3102
Undetermined.....	Traces

**History.** — To write a full account of the important part played by water in the history of chemistry would be to write a history of chemistry. Some points, however, stand out prominently. Apparently, Cavendish, 1784, first synthesized water by burning hydrogen, and Lavoisier analyzed it by decomposition with red hot iron. In 1800, Nicholson and Carlisle first decomposed water by means of the electric current.

The importance of the relative weights of the constituents of water will be clear, even to the beginner, but its full significance will grow upon the student. It is, therefore, of interest to call attention to two classic investigations upon the subject. In 1842, Dumas determined exactly the relative amounts of hydrogen and oxygen in water by passing hydrogen over carefully weighed copper oxide, and weighing the water produced. His results were 5.54 grams of hydrogen, 44.22 grams of oxygen, which is a ratio of 2.0045 : 16. This ratio is a little high, as has since been determined, by reason of the occlusion of hydrogen by the reduced copper. In 1895, E. W. Morley, of Adelbert College, Cleveland, finished a series of

determinations of the weight relations of hydrogen and oxygen in water, which was so painstaking and accurate as to be considered a model and is at present the last word on the subject. His results give the ratio as 2.016 : 16. (His paper is published by the Smithsonian Institution.\*)

In 1805, Humboldt and Gay-Lussac investigated carefully the combining ratio by volume of hydrogen and oxygen, which was

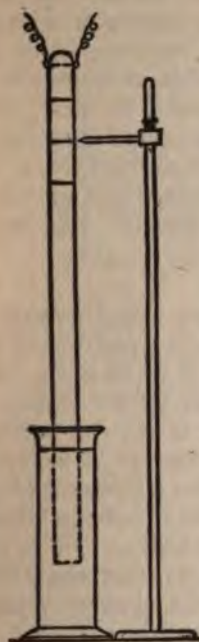


FIG. 23.

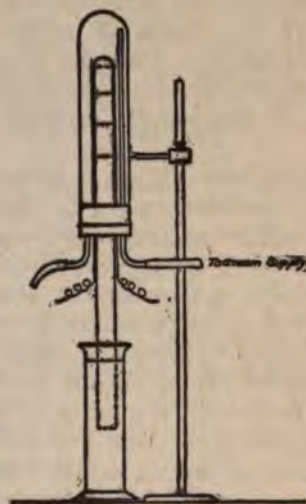


FIG. 24.

shown by Cavendish's synthesis to be about two of hydrogen to one of oxygen, and by the decomposition of water by electricity to be rather more than two to one. The results of their experiments, which were performed in an apparatus very similar to that described by Fig. 23, showed the relation of 1 vol. of oxygen to 1.9989 vol. of hydrogen, or almost exactly 1:2. If the experiment be conducted so that the steam formed be kept

\* See also Am. Jour. Sci. 41, 220 and 276.



at the same temperature and pressure in an apparatus such as shown in Fig. 24, the volume relation of steam is found to be the same as that of the hydrogen used. Gay-Lussac followed up this investigation, with the remarkable result that a similar simple relation was found between the volumes of all gases which combine. The relation is very important, because of subsequent use in chemical systematization, and is known as Gay-Lussac's Law of Combining Volumes. It may be stated: **When gases unite the volume relations of all gaseous factors or products can be expressed by small whole numbers.** This rule holds, even as Boyle's Law and Charles' Law, only approximately, but is of none the less importance for that reason. Scott, in 1893, found as the result of a very careful series of experiments that the volume relation of the union of oxygen and hydrogen is 1:2.00245. Morley's ratio is 1:2.00269. The variation of the gas laws from exact integral relations finds explanation through Van der Waal's equation (*cf.* Bigelow, Theoretical Chemistry, p. 155).

**Purification.** — Since pure water is not found in nature, it is frequently essential to purify that which is available to make it suitable for the particular use to which it is to be put. Thus, if a city is forced to use a given stream or lake for its supply and the water is either non-potable or unsanitary, it may be purified sufficiently for practical purposes in one of a number of ways. If it is desired to remove suspended matter, which may consist of particles of clay or other earthy matter, the supply may be dammed or a large reservoir built and, the water being so kept at rest for a time, the solid material for the most part sinks to the bottom, since the carrying capacity of flowing water varies as the square of the speed. The process is called **sedimentation**. The water may also be separated from suspended matter by **filtration**. This method is used in a wide variety of modifications from the simple unglazed porcelain tube designed to fit on the faucets of the household supply, sometimes known as Pasteur or Pukall filters, to the enormous beds of sand and crushed rock suitable for the great supplies of cities. A modification which not only removes solid substances, but also coloring matter and dissolved gases, probably by occlusion, is furnished by the charcoal filter. If it be desired to remove the living organisms present, *e.g.*, disease germs, the result is sometimes obtained by **disinfection**, either by bleaching powder (*q.v.*) or by ozone (*q.v.*) or by subjecting the water to the action of power-

ful ultraviolet light (see Sci. Am. Sup., vol. 79, p. 10).<sup>\*</sup> The latter method illustrates also the germicidal effect of sunlight. Neither sedimentation, filtration nor disinfection in any way tends to remove dissolved material. This result may be obtained by **distillation**, which consists in converting the water to steam and condensing again by means of cooling jackets. The laboratory device for this purpose is illustrated by Fig. 25. When water is

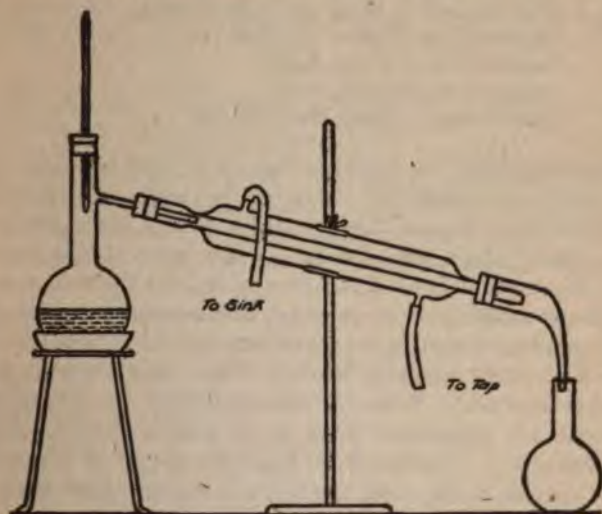


FIG. 25.

heated the dissolved gases pass off first and if care be taken to keep the water subsequently distilled out of contact with air, the water will be practically free from gas and, if the distillation is stopped before volatile solids are driven off, the only foreign materials present are such traces of the containing vessels as may be dissolved. Distilled water sufficiently pure for laboratory purposes can be made by using glass condensers and containers, but if specially pure water is desired, platinum apparatus is used.

<sup>\*</sup> Emergency purification of polluted water is sometimes accomplished by electrolysis. The impure water contains sufficient chlorides so that by electrolysis, and subsequent stirring, hypochlorites are produced (see Labarraque's solution, p. 191). Some ozone is also produced.



**Physical Properties.** — The properties of water of greater importance to chemistry may be tabulated and certain of them discussed:

Colorless.

Odorless.

Tasteless.

Specific gravity at 0° C. = 0.99987; 4° C. = 1. }

Specific gravity, solid, at 0° C. = 0.9167.

Specific gravity, vapor (air = 1) = 0.622.

Boiling point = 100° C.; 212° F.

Specific heat = 1 (standard).

Latent heat of fusion, 79 cal.

Latent heat of evaporation, 537 cal.

Water is described as colorless, odorless, and tasteless, but this refers to the pure substance. Ordinary water is colorless if in thin layers, but if light passes through thick layers the color seems to be a deep blue, which may be due to the color of the water or to the effect of suspended particles on the light. Since most natural water is more or less yellow in color, frequently the thicker layers offer the resultant color, green. Of course, if all incident light is absorbed the water appears black; hence, the varying colors of rivers, lakes and sea. Water is odorless until contaminated with some odoriferous substance, such as hydrogen sulfide. Likewise, the pure substance is tasteless if free from dissolved materials, but since such is seldom the case, the taste of water varies according to

the source of the supply. Ordinarily the taste is due chiefly to dissolved gases.

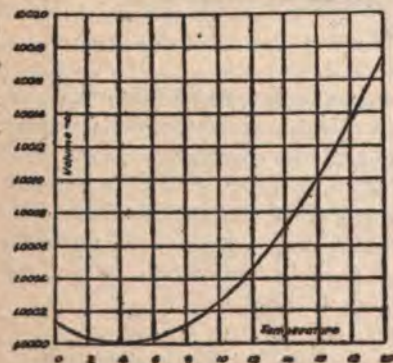


FIG. 26.

The curve showing the change of density with change of temperature is given in Fig. 26. The point of maximum density is 4° C. One liter at 4° C. occupies

**Specific Gravity.** — Water has been used as a standard for the measurement of the relative weight of solid and liquid substances, at least since the time of Archimedes and his famous determination of the sophistication of the crown of Hiero of Syracuse. Water expands and contracts with change of temperature and hence a definite temperature must be designated to accurately define the unit of specific gravity.

13 cc. at  $0^{\circ}\text{C.}$ , 1001.8 cc. at  $20^{\circ}\text{C.}$ , and at  $100^{\circ}\text{C.}$ , 1043.4 cc. When at  $0^{\circ}$  changes to ice at the same temperature the increase in volume is approximately 10 per cent. This change has far-reaching geological, cultural and architectural consequences, which are matters for study in other connections. The unit conveniently used for the gravity of gases is air taken as unity. Water vapor, then, is times as heavy as air. Since air weighs 1.293 grams per liter, liter of water vapor at  $0^{\circ}\text{C.}$  and 760 mm. weighs 0.8045. 1000 s of water (1 l. at  $4^{\circ}\text{C.}$ ) would, therefore, occupy approximately l. at  $100^{\circ}\text{C.}$ , if converted into gaseous form at that temperature.

**Specific Heat.** — Water is also used as a unit in the measurement of relative heat capacities of solids and liquids. The amount of heat required to raise one gram of water one degree Centigrade is called a *calorie*, and since the specific heat varies slightly with the temperature usually specified is the interval between  $15^{\circ}$  and  $20^{\circ}\text{C.}$ . In technical work in the United States and the British Empire, the unit of specific heat commonly used is the amount of heat required to raise one pound of water one degree Fahrenheit between the interval  $63^{\circ}\text{F.}$  to  $64^{\circ}\text{F.}$ . This is known as the British thermal unit (B.t.u.). The relation between the calorie and the c.g.s. unit of energy, the erg, is  $1 \text{ cal.} = 41,890,000 \text{ ergs.}$  or 4.189 joules. (For details of the relative values consult the appendix.) When ice is converted from  $0^{\circ}\text{C.}$  to water at the same temperature, 79 cal. of heat per gram of ice are required to effect the change. This is known as the latent heat of fusion. Similarly, to convert water from the liquid condition at  $100^{\circ}\text{C.}$  to steam at the same temperature requires 537 cal. per gram. This is known as the latent heat of vaporization. These properties of water are only in degree from the like properties of other substances in passing from the solid to the liquid and gaseous conditions and may be regarded as typical. It follows then that substances in the solid state possess less potential energy in the solid than in the liquid and still less in the gaseous state.

The reader having an elementary acquaintance with physics is already aware that in measurement of heat we deal with two factors, the quantity of heat and the differences in intensity of heat of bodies. The latter is known as temperature and the usual method of comparison is by means of measuring the increase or decrease of the volume of substances with change of temperature. In any such comparative measurements arbitrary units must be selected. The ordinary fixed points for temperature are the freezing point of water and the boiling point at 760 mm. pressure. The scientific fraternity the world over, and the public in all countries, employ for the purpose the centigrade thermometer, which uses as the melting point of ice, or in the phraseology of the phase rule (*q.v.*) the point of equilibrium between ice and water when in contact with each other. The other

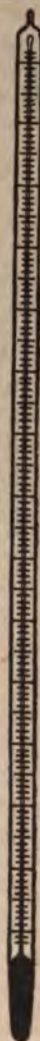


FIG. 27.



fixed point is similarly the equilibrium point between water and water vapor when the pressure of the latter is 760 mm., which is called 100°. If a fixed weight of some liquid or gas is enclosed in a suitably shaped vessel, the whole immersed in melting ice, the volume occupied marked 0, then transferred to boiling water, the volume again marked at 100, the volume expansion divided into one hundred divisions and the vessel graduated above and below these marks in divisions of the same value, we have the essentials of a thermometer. The ordinary type used is shown in Fig. 27. The substances usually employed as registers of the volume change are mercury or alcohol, though many other substances may likewise be employed. The centigrade scale is sometimes called, from its inventor, the Celsius scale. Fahrenheit likewise employed water as his fixed points, but selected as the freezing point the value 32 and as the boiling point 212, thus dividing the volume expansion between these values into 180 parts, and continuing the same scale above and below the fixed points. Reaumur likewise employed the fixed points of water, but used only 80 divisions on his scale.

For detailed discussion of the history of thermometry the reader is referred to a little book called the "History of Thermometry," by Bolton, and for details of the accurate calibration of thermometers, to works on the laboratory operations of physics and physical chemistry, *e.g.*, Ostwald-Luther.

**Vapor Tension.** — If a perfectly dry tube, a meter or more in length, be filled with mercury and inverted in a vessel of mercury, the level at which the liquid in the tube will stand depends upon the weight of the atmosphere. If the level be marked and a few drops of water introduced, the level of the mercury will fall and the apparently empty space in the tube will be increased. If now the tube be surrounded by a vessel so that the upper end may be immersed in water of varying temperature, the height of the mercury will be seen to decrease the higher the temperature of the surrounding water. See Fig. 28. It is clear that something is tending to balance the external air pressure, and if the space above the water be examined by proper methods it will be found to contain water in the form of vapor. If the measurements are carefully made and the results tabulated, the pressure exerted in the tube by the vapor will

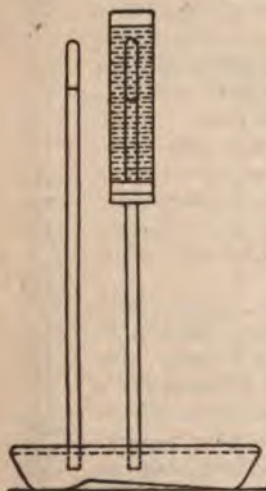


FIG. 28.

be found to correspond to those tabulated under the heading **aqueous tension** in the appendix. It will be observed that

the vapor tension is a fixed quantity for a given temperature. This property is not peculiar to water, since ice also exerts a definite though small vapor tension, which, indeed, is the same as that of water at  $0^{\circ}$  C. Other substances, also, such as camphor, ammonium carbonate, alcohol, ether, etc., show the same tendency to marked degrees. Indeed it is probable that all substances tend thus to pass into gaseous form at all temperatures, though in many cases measurement is practically impossible because of the small magnitude of the values. To this tendency to vaporize is traceable the spontaneous evaporation of liquids at all temperatures, yet it must not be inferred that the change does not require energy. To vaporize water requires the absorption of a quantity of heat by so much greater than 537 cal. per gram as the temperature is below  $100^{\circ}$  C. The necessary heat in the case of the colossal operations of nature is supplied by the sun. Of course, when the vapor is again condensed to liquid water, the absorbed heat is again liberated.

It will be observed that the terms gas and vapor are used interchangeably. The distinction at one time maintained was to term a substance in the gaseous condition a vapor when by cooling it could be condensed to the liquid condition. As will be seen when the subject of liquefaction of gases is considered, this is true of all gases, provided the cooling be sufficient, hence it is impossible, as well as unnecessary to draw a sharp dividing line in the use of the terms. Conventionally, we use the term vapor when speaking of easily condensable gases.

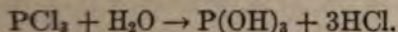
As we have seen, if a liquid is enclosed in a limited space the amount of vapor formed is limited at a given temperature by the pressure produced. If in any way the quantity of vapor is increased, *e.g.*, by introduction of vapor from an external source, some vapor condenses so that the pressure may remain constant. When a liquid is exposed in an open vessel the gas escaping cannot ordinarily accumulate to an extent which will produce the maximum pressure, because of diffusion and of the mechanical action of air currents, and hence the evaporation continues so long as any liquid is present. It will be observed then that rapidity of evaporation at a given temperature is favored by withdrawing the vapor produced, by means of an "air pump" or by currents of air blown across the surface. The explanation of these facts which has been found most satisfying to the normal scientific mind is found in the kinetic molecular hypothesis which will be presented in Chapter V.



**Boiling Point.**—Reference to the table of vapor tension of water will show that at  $100^{\circ}\text{C}$ . the vapor tension of water equals the pressure of the atmosphere and since but little added energy will suffice to enlarge the space available for the vapor, rapid formation of vapor will take place, provided the heat needed for vaporization be continually supplied. This rapid vaporization takes place in the body of the liquid and the bubbles of water vapor rising through the liquid produce the familiar phenomenon called boiling. It will be observed that the temperature at which this takes place is dependent upon the temperature at which the vapor tension is equal to the gaseous pressure upon the liquid. If, therefore, this pressure be increased the boiling point rises; thus in a steam boiler water boils at  $121^{\circ}\text{C}$ . when the pressure is 29.4 lbs. per square inch, or the equivalent of twice the pressure of normal atmosphere (2 atmospheres), at  $180^{\circ}\text{C}$ . when the pressure is 10 atmospheres, and at  $374^{\circ}\text{C}$ . when the pressure is 200 atmospheres. Conversely, if the pressure is below the normal atmospheric pressure, the boiling point of water is lowered. For example, at high elevations where the normal barometric height is low, the boiling point is correspondingly low. Thus, at the University of Wyoming the normal barometric height averages about 23 inches and the boiling point is  $92.5^{\circ}$ . If by aid of an exceptionally good air pump, water is rapidly evaporated at a pressure of 4 mm., it will freeze and boil at the same temperature. Other physical properties of water will later claim attention.

**Chemical Properties.** 1. **Decomposition.**—When water is formed by burning hydrogen, 68,000 cal. of heat are produced per formula weight in grams. The heat of formation of a compound is a rough measure of its stability. Few compounds are more stable than water, since relatively few have so great heat of formation. If water is decomposed, a corresponding amount of energy is absorbed. It is not sufficient that a given amount of energy be available; it must be used under suitable conditions. If water is heated to a **sufficiently high temperature**, it should decompose into its elements. At a temperature of  $2500^{\circ}\text{C}$ ., the decomposition only amounts to about 4% when the products of decomposition are not removed, *i.e.*, if the water be heated in a closed system. At ordinary temperature water may be decomposed by electrolysis. It is also decomposed at low, or but relatively slightly elevated, temperatures by contact with certain metals or with carbon (*cf.* pp. 54 and 349).

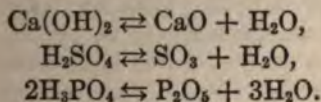
**2. Double Decomposition.** — Certain compounds when treated with water react as indicated in the following equation.



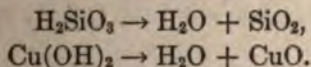
This type of reaction is known as **hydrolysis**. We shall meet with many instances of it. The explanation of the mechanism of the process will receive fuller explanation when certain additional tools of our trade are in our hands (*cf.* Chapter IX).

**3. Addition Products of Water.** — As has been mentioned (p. 70) water can be obtained by heating many substances which are apparently dry. These substances present a series of compounds which illustrate very strikingly the difficulties of arbitrary classification.

Certain compounds, *e.g.*, sugar or starch, when heated sufficiently are decomposed, water being one of the products. Thus cane sugar  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{C} + 11\text{H}_2\text{O}$ . If, however, we place carbon and water together, we have no indication of a tendency to combine to form sugar. Another group of substances likewise yields water if heated sufficiently, but if the products of the decomposition are allowed to interact, the original substances are produced. Examples of this group are slaked lime,  $\text{Ca}(\text{OH})_2$ , sulfuric acid,  $\text{H}_2\text{SO}_4$ , phosphoric acid,  $\text{H}_3\text{PO}_4$ . The relation may be indicated by the following equations:



Intermediate between these two groups we find substances which react on heating just like slaked lime or sulfuric acid, but the products show little inclination to interact. Examples are furnished by silicic acid and copper hydroxide:



In all the above cases, a careful study of the compounds seems to show that the water is not present as such but is produced on heating. This is made clear by their structural or constitutional formulae (p. 200). In such compounds we regard the hydrogen and oxygen as **water of constitution**. In none of these compounds is there an appreciable vapor tension.



There is, however, a group of compounds which if inclosed in a Torricellian vacuum (Fig. 28), will lower the mercury column to varying degrees. That is, they show a vapor tension. They appear dry, however. When heated, they lose moisture more readily than when at lower temperature. Most such substances are crystalline and when water is removed from them, the crystals lose their shape and color, if originally colored. These substances are said to contain **water of crystallization**. In this group of substances, it also appears that water is not present as such but is **formed by decomposition**. It is, however, usual to indicate their instability by the use of the term **hydrate** in describing them and to write their formulas in a form which indicates this relation. Thus we may speak of blue vitriol as the **hydrate** of copper sulfate and we ordinarily write its formula  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Its composition would be correctly expressed  $\text{CuH}_{10}\text{SO}_9$  but such a formula would not indicate the **hydrate** character of the substance. Other common hydrates are crystalline borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , ordinary alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , copperas,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Hydrates when exposed to the air sometimes have so great a tendency to lose water of crystallization that they lose their crystalline form and become opaque powders. Such crystals are said to be **efflorescent** (**efflore** = to become like flour). Examples of such hydrates are Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , sodium thiosulfate (Hypo),  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and washing soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . Other hydrates remain unchanged in ordinary air apparently because their tendency to lose water is counteracted by the presence of water vapor in the air. An example is blue vitriol,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Still other hydrates are capable not only of retaining all their water of crystallization in the presence of moist air but even attract moisture from the air, at times in sufficient quantities to make a product which is liquid. Such substances are said to be **deliquescent** (**de-liquore** = to become liquid). Examples are hydrated calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and potassium carbonate,  $\text{K}_2\text{CO}_3$ .

Practically all substances appear to be capable of attracting **some** moisture from the air. When such attraction is not sufficient to produce liquefaction, the substances are said to be **hygroscopic** (from *ὕγρός* = moist and *σκοπεῖν* = to view).

This property is so nearly universal that it is scarcely an exaggeration to say that all solid material in ordinary air is covered with a film of moisture. Many laboratory operations are complicated by the presence of hygroscopic moisture.

Especially is the exact weighing of vessels rendered difficult because of the presence of quantities of hygroscopic moisture, which quantities vary with the temperature and humidity of the air. One of the most frequently employed devices to obviate such difficulties is known as a desiccator (from *desiccatus* = to dry). This is a closed vessel containing a substance which is strongly hygroscopic or deliquescent so that the water vapor in the air space above it may be maintained at a constant concentration (see Fig. 31).

An explanation of efflorescence and of deliquescence in terms of the kinetic molecular hypothesis will be offered when that topic shall have been presented. See Chapter V.

**4. Solution.** — On p. 14 attention was called to solutions as a group of substances intermediate in character between compounds and mixtures. It now becomes necessary to define the term more accurately. It is a matter of ordinary experience that many substances when brought into contact with water disappear as such and produce a homogeneous liquid which, while resembling water, has acquired additional properties. Thus, if a small quantity of salt be placed in water, the resulting homogeneous liquid has acquired a characteristic taste, has become a conductor of electricity and does not freeze at  $0^{\circ}\text{C}$ . or boil at  $100^{\circ}\text{C}$ . This sort of combination may take place between substances in either the liquid, solid or gaseous state. We may define a solution as a homogeneous mixture of two or more substances, the relative proportions of which may vary continuously between certain limits and the properties of which vary with the proportions of the components.

The process of forming a solution is to be regarded as a mutual act taking place between the components. For convenience, however, we usually speak of one substance called the *solute*, as dissolving in another, the latter called the *solvent*. It is quite immaterial which of two components is called solute and which solvent though ordinarily the component present in larger quantities is called the solvent. Thus, in a solution of salt in water, the latter is regarded as the solvent. It is quite impossible at times to assert positively whether a given solution is a chemical compound of solute and solvent or is a mixture of the two.

Solutions are of great importance to the chemist since either from choice or necessity he so frequently employs them in his operations. (This importance may perhaps be emphasized by quoting the alchemistic proverb; "Nothing reacts except in solution," even though it is not strictly true.) The properties of solutions



are so varied and of such importance that a special chapter (Chapter IX) will be devoted to them. Certain items concerning aqueous solutions particularly are presented here because of the necessity for their immediate use.

**Solids and Water.** — If we add to a fixed quantity of water successive small quantities of a solid substance, *e.g.*, common salt, we find that the solid dissolves at first, if the initial addition is sufficiently small. With successive additions, we reach a point at which no more will dissolve and we have solid material in excess. If we measure the quantity dissolved, we find that it varies markedly for different substances, but for each substance there is always a fixed quantity which will dissolve at a given temperature. When a fixed quantity of solvent will dissolve no more of a solute while in contact with the latter, we have a saturated solution. The quantity of a substance required to make a saturated solution is known as its solubility. It is usual to express this quantity in grams per liter or in gram molecular weights per liter, though other modes of expression are also employed. When a substance dissolves to a very considerable degree, we speak of it as a soluble substance. Some quantity of practically all substances dissolves in water, yet in many instances the solubility is so small that for many practical purposes it may be ignored. Such substances are often called insoluble. To an aqueous saturated solution, water may be added *ad infinitum* without other apparent change than a gradual diminution of the characteristic properties due to the presence of the solute. Thus, while we have a maximum limit of solubility, there is no limit to dilution. We ordinarily speak of a solution which is relatively far from saturated as a dilute solution.

The usual effect of increased temperature is to increase the solubility of solids in water. The rate of increase is variable, depending upon the character of the solute. In some cases, the solute becomes less soluble with increase of temperature. A convenient means of showing the relation between temperature and solubility is by use of curves in which change of temperature is indicated on one axis of a coordinate system and solubility on the other. A number of such curves are given in Fig. 29. It will be observed that in some cases degree of solubility is but slightly affected by change of temperature.

Some very interesting consequences follow from the change of

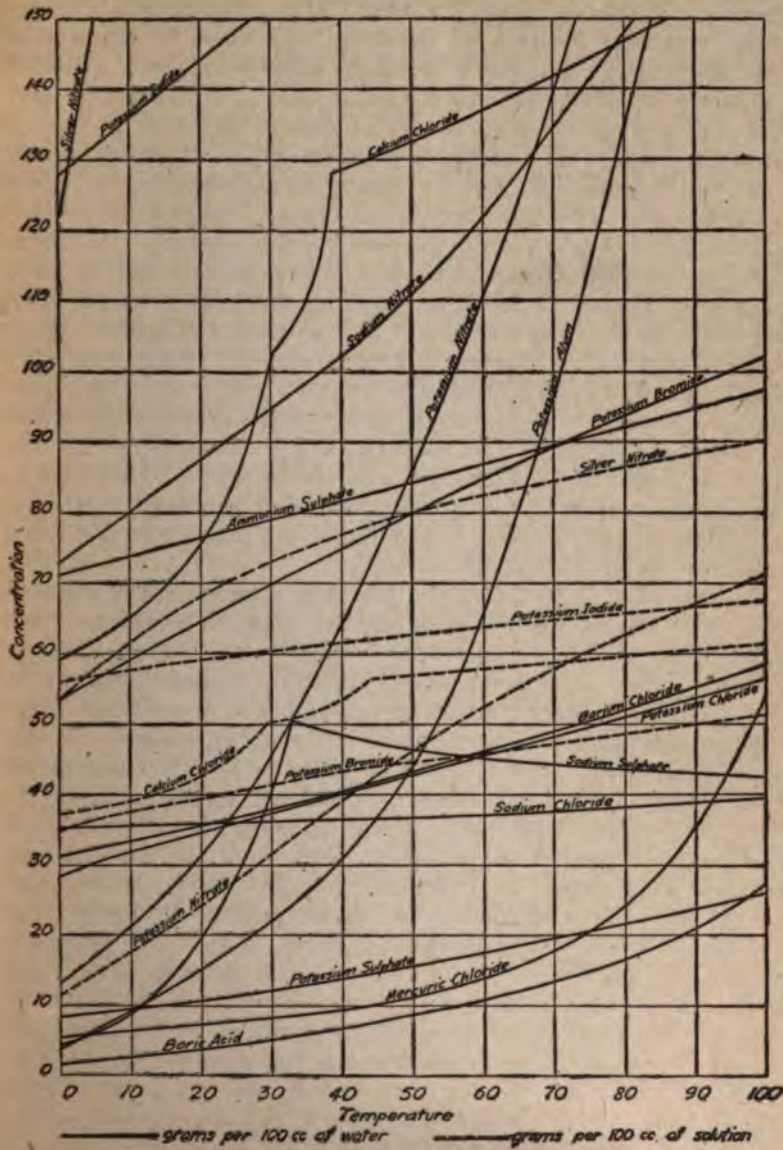


Fig. 29.



solubility with change of temperature. If a saturated solution of a substance more soluble in hot than in cold water be made at a given temperature and the solution decanted or filtered to free it from solid material, and then cooled, one of two results may follow. The material in excess of the amount required to form a saturated solution at the lower temperature may separate out. It ordinarily appears in definite regular forms called crystals (see crystal forms). The same process, of course, occurs when a saturated solution is allowed to evaporate spontaneously. In some cases, however, the excess material may not separate out on cooling and we thus have a **solution containing more dissolved material than could be taken up by contact with an excess of solute**. Such solutions are called **supersaturated** solutions. Supersaturation usually occurs with substances which can form hydrates. A supersaturated solution may be caused to deposit its excess solute either by violent agitation of the solution or by inoculation. By the latter, we mean the addition of some of the solute in solid form. Explanation of some of the facts regarding supersaturation and crystallization can be offered in terms of the phase rule (*q.v.*) and the kinetic molecular hypothesis (*q.v.*).

In general, it is true that **the presence of one solid in solution in no way affects the solubility of the other substances**. This statement is subject to considerable modification as we shall see (*cf.* Chap. IX). It is, nevertheless, important to know that a solution may contain several dissolved substances at one time and that in general the presence of one does not materially affect the behavior of another. Use is made of this fact to effect separation of substances from each other by **fractional crystallization**. An illustrative case may be cited. Let us suppose we have a solution saturated with respect to potassium perchlorate ( $\text{KClO}_4$ ), but unsaturated with respect to potassium chloride ( $\text{KCl}$ ). If this solution be allowed to evaporate, as water passes off the crystals produced at first will be of perchlorate only. Eventually, of course, the solution will become saturated with the chloride after which further evaporation results in the deposition of both salts. If, however, the crystallized material be removed in separate portions as the operation continues, the first fractions will be pure perchlorate, or at worst contain more perchlorate than the original mixture from which the solution may have been made. Extensive use is made of fractional crystallization in the purification of substances.

**Water and Other Liquids.** — In case the solute is a liquid, the same facts are found to obtain as with solids except in some instances there is no limit to the solubility, *e.g.*, a homogeneous mixture results when water and alcohol, or water and sulfuric acid are mixed regardless of the relative amount of each. Such pairs of liquids are said to be miscible in all proportions. In these cases it is particularly apparent which component is to be called solute and which solvent is optional.

**Water and Gases.** — The limit of solubility of gases in water depends upon the gaseous pressure. At a given pressure, the solubility varies within wide limits for different gases. Thus hydrogen at 0° and 760 mm. dissolves only to the extent of 2 cc. per 100 cc. of water, while under the same conditions, the solubility of ammonia is 114,800 cc. to 100 cc. of water. With a given gas, the solubility varies directly as the pressure, *e.g.*, if the solubility of a gas is  $a$  at a pressure of one atmosphere, 760 mm; at two atmospheres, the solubility is  $2a$ ; at half an atmosphere,  $\frac{1}{2}a$ , etc. This law was discovered in 1803 and, from the name of its discoverer, is known as Henry's law. Unfortunately, it obtains only for relatively slightly soluble gases. At about the same date, 1802, Dalton observed that in a mixture of gases which do not react chemically with each other each gas exerts the same pressure as if it alone occupied the entire vessel and the total pressure is the sum of the partial pressure due to each gas. This is known as Dalton's law of partial pressures. It follows, then, that from a mixture of gases, each gas dissolves independently to an extent dependent upon its partial pressure. The general effect of rise of temperature is to diminish the solubility of gases in water and except in certain special cases (*cf.* hydrochloric acid) the solubility becomes nil at 100° C.

**Measures of Concentration of Solutions.** — The solubility, and also the concentration of unsaturated solutions, of substances in water is variously expressed. Where weight relations only are of paramount interest, we may state the number of grams of solute per 100 cc. or 1000 cc. of solvent, or the weight in grams per 100 or 1000 grams of solution. The latter is the usual method employed by the pharmacist or the physician. When chemical units are employed, two methods are in use one of which is based on the formula weights and the other upon chemically equivalent quantities. The former are called molar solutions, the latter



normal solutions. A molar solution may be defined as one which contains a formula weight in grams of a solute in a liter of solution; *e.g.*, a molar solution of sulfuric acid is one which contains 98 grams of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) per liter of solution.

A normal solution is one which contains enough of the solute per liter to be chemically equivalent to one gram of hydrogen. Thus a normal solution of sulfuric acid,  $\text{H}_2\text{SO}_4$ , will contain 49 grams of sulfuric acid per liter since for chemical purposes the acid contains in 98 grams, a formula weight, the equivalent of two grams of hydrogen.

We may then express the concentration of solutions as multiples of fractional parts of molar or normal concentration. For example, a solution containing 3.65 grams of hydrochloric acid ( $\text{HCl}$ ) is said to be to either tenth molar,  $m/10$ , or tenth normal,  $n/10$ . For certain purposes, one system of measures is convenient, for other purposes, the other system serves better. The student may await experience to learn when to use each.

**Continuity.** — As was mentioned on p. 2, nature often presents continuous series of phenomena which merge gradually from one distinct phase into another. This is sometimes called the **law of continuity**. For convenience of study, and discussion, it is often desirable to subdivide such continuous series into separate groups. This process, while useful and indeed essential, always encounters the difficulty that at the artificial boundary lines established there are found phenomena difficult to classify. We have been dealing with a case of this sort. Water has been shown to be related to many substances in ways which have been distinguished as (a) **hygroscopic moisture**, where the water seems to adhere to the surfaces only and no chemical relations appear to obtain; (b) "water of solution," where aqueous, *i.e.*, watery, character seems to predominate; (c) "water of crystallization," where definite chemical combination appears to obtain but in which at ordinary temperature the aqueous tension can be observed; and (d) "water of constitution," where even aqueous tension only appears to manifest itself at higher temperatures which range all the way from slight to great elevations. On the border line between these classes of water combinations, we must expect cases difficult to place. Thus we may ask, without expecting definite answer, whether the water absorbed by a deliquescent substance like calcium chloride is water of solution or water of crystallization.

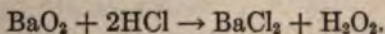
Other instances of continuity will be mentioned in subsequent pages.

**Uses of Water.** — The reader most innocent of acquaintance with chemistry is of necessity familiar with the obvious indispensability of water in the human economy as a beverage (in spite of the observation of Aristotle that great caution in this direction is to be observed), as a cleaning agent, as a vehicle for foods and for commerce; and must have also, from physical geography or other experience, some appreciation of its importance in determining geological and climatic conditions and in agriculture. It is of equal importance in chemistry. The behavior of substances in water is so radically different from that in its absence, and its presence as liquid, vapor or hygroscopic water is so prevalent that it is essentially the central or pivotal substance in chemistry. The truth of the above statement will come home to the reader more forcibly as he continues the subject.

#### HYDROGEN PEROXIDE

There exists a substance other than water containing only hydrogen and oxygen. It is known as hydrogen peroxide. It occurs in minute quantities in the air and is formed to a very small extent when hydrogen is burned and the products are suddenly cooled. The satisfactory discussion of its properties is not easy at present for reasons which will enforce the need, which is already severely felt, of some more efficient aid to our systematization of facts than the facts themselves. (See molecular weights, p. 99.)

**Preparation.** — Hydrogen peroxide was first prepared in 1818 by Thenard, who treated barium peroxide with ice cold hydrochloric acid. The reaction may be expressed,



He was able to remove the barium chloride formed by treatment of the solution with silver sulfate in exactly equivalent amount.  $\text{BaCl}_2 + \text{Ag}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{AgCl}$ . Since both products are insoluble, by filtration a solution was obtained which had properties very distinct from those of water, and yet was composed only of hydrogen and oxygen.

Commercially, hydrogen peroxide is prepared by adding to a mixture of sulfuric acid and water in equal proportions, which is



kept below zero by a freezing mixture, a quantity of barium peroxide sufficient to neutralize the acid. The mixing is best performed

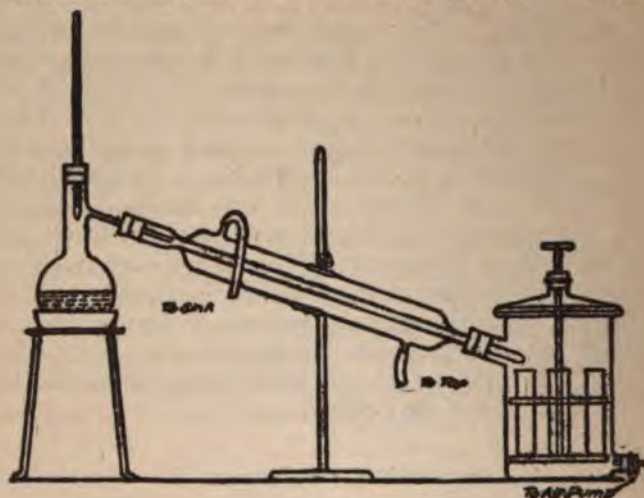


FIG. 30.

by suspending the barium peroxide in water, by thorough shaking, and stirring this mixture into the acid. After standing until the reaction is complete, the barium sulfate is filtered out and the solution is carefully evaporated at a low temperature,  $70^{\circ}$  or below,



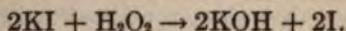
FIG. 31.

until a solution of the desired concentration is obtained. If it is desired to obtain a solution more concentrated than 40 per cent, the evaporation must be carried out by distilling under diminished pressure, as illustrated in Fig. 30. In this manner, a solution of nearly pure hydrogen peroxide may be prepared. The last traces of water may be removed by allowing to

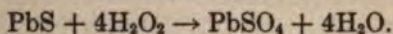
stand over sulfuric acid in a vacuum. This operation is illustrated in Fig. 31. The pure material is so unstable that for commercial purposes a 3 per cent solution is ordinarily employed. Hydrogen peroxide is also frequently formed when substances are slowly oxidized in the presence of moisture.

**Physical Properties.** — The pure peroxide is a colorless and odorless liquid somewhat more viscid than water and with a metallic, unpleasant taste. Its boiling point at atmospheric pressure is unknown, since it decomposes rapidly when warmed. At 68 mm. pressure its boiling point is 85° C. The melting point is -2°. It is miscible with water in all proportions.

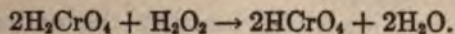
**Chemical Properties.** — The pure peroxide decomposes very rapidly into water and oxygen in the presence of light, finely divided metals, manganese dioxide, and other catalytic agents, such as dust, rough surfaces, etc. The substance is usually kept for use only in dilute solution and our interest is mainly in the properties of this. The concentration is sometimes expressed in the percentage by weight of peroxide present and sometimes in the volume of oxygen furnished by its decomposition. A three per cent solution will give about 10 times its own volume of oxygen and hence is called a ten volume solution. The solutions are sold under various trade names, such as proxhyde, perhydrol, dioxygen, etc. The stability of the solution is increased by being kept in brown bottles and by addition of preservatives, *e.g.*, acetanilide. A solution of hydrogen peroxide added to a solution of potassium iodide liberates iodine according to the equation:



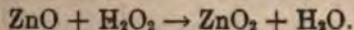
The reaction is facilitated by addition of ferrous sulfate and also by addition of acids. It also oxidizes lead sulfide to lead sulfate.



It bleaches hair, straw, feathers, silk, teeth, indigo, etc., by oxidizing the coloring matter to colorless or less highly colored substances. In particular, it oxidizes chromic acid to perchromic acid and the blue compound formed is more stable in ether than in water. With some reservation, the reaction may be written (see perchromic acid):



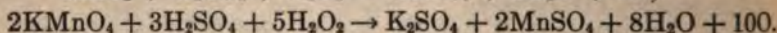
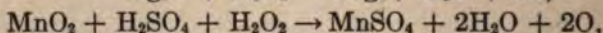
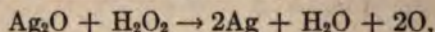
The blue solution perhaps contains  $\text{Cr}_2\text{O}_7$ , but in any case its formation is the most delicate test for the presence of the peroxide. Many oxides are converted into peroxides by treatment with hydrogen peroxide, thus,





The peroxides so formed find various but limited uses in medicine.

The most striking behavior of hydrogen peroxide is in its reactions with certain substances, themselves powerful oxidizing agents. A few illustrative reactions follow:



Hydrogen peroxide is an endothermic compound, that is, it has a negative heat formation and consequently when it decomposes, heat is liberated. The quantity per formula weight in grams is 23,100 cal.

The question, of course, has risen in the mind of the reader as to the reason for writing the formula of hydrogen peroxide as  $\text{H}_2\text{O}_2$ , when in the interest of simplicity it apparently should be  $\text{HO}$ , since the latter expresses the weight relation of the constituents exactly. The question will be answered very shortly (see p. 99).

**Uses.** — As intimated previously, hydrogen peroxide is used extensively as a disinfectant and as a bleaching agent. In both capacities, its usefulness is due to the ease with which it liberates oxygen (see p. 91) and the consequent results of the activity of the "nascent" oxygen. The activity is, of course, more to be expected when we consider the liberation of energy involved in its decomposition.

**Exercises.** — 1. Describe the cycle of water in nature.

2. Make a list of all the varieties of water which are described in the text and state what gives to each variety its name.

3. If in Dumas' determination of the composition of water he had used 200 grams of cupric oxide, what volume of hydrogen must have been required?

4. In case you desired to ascertain the correctness of Gay-Lussac's law of volumes for hydrogen and oxygen in the formation of water, and the maximum temperature available was  $92^\circ\text{C}.$ , what would be the maximum pressure at which the volume relations could be observed?

5. Write a brief account of the water supply of your home town, detailing (a) source, (b) type of water, (c) purification.

6. If a substance has the specific gravity of 10.7, what will be the weight of 60 cc. of it and what volume of water at 100° will weigh the same?

7. If 1700 cc. of water vapor at 100° C. and 760 mm. pressure are formed from 1 gram of water, what volume would it occupy at 0° C. and 760 mm., provided Charles' law obtained throughout? What weight would a balloon filled with 1000 grams of water vapor lift, assuming the air to be 0° C. and 760 mm. and the vapor to be 100° and 760 mm.?

8. Calculate the thermal value of hydrogen in B.t.u.

9. Calculate the temperature in the Centigrade scale and the absolute scale when the Fahrenheit reading is 5°.

10. If the vapor tension of water vapor in a room is 23 mm., and the temperature of the room falls to 20° C., how much condensation occurs, provided the room be  $20 \times 10 \times 10$  meters?

11. How much water is needed to slake 10 grams of lime?

12. Make an outline of the effect of temperature on the solubility of solids, liquids and gases in water.

13. Make a list of the personal uses to which you have put water during the preceding 24 hours. Include, of course, all operations in which it is a part.

14. Assuming no escape of heat and a specific heat of 1 for the solution, calculate the rise of temperature of an insulated solution of 100 grams of a 10 per cent solution of hydrogen peroxide when decomposed.

15. The relative humidity of air at a given temperature is the ratio of the observed vapor tension ( $f$ ), to the aqueous tension of air saturated with water vapor ( $F$ ), i.e.,  $f/F$ . The vapor tension of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  being 2 mm. at 9° C., what must be the relative humidity of air, to prevent efflorescence?



## CHAPTER V

### KINETIC-MOLECULAR AND ATOMIC HYPOTHESES

"We must educate ourselves to regard the ideas or theories as the changing part of science and keep ourselves ready to accept even the most fundamental revision of current theories." — Ostwald.

**Purpose of Hypotheses.** — In the discussion of the topics dealt with in the preceding chapters, we have avoided answering certain rather obvious questions because of inability to give answers in terms of fact (*cf.* pp. 17, 49, 92). When such questions present themselves the scientist may deal with them in various ways. He may cry "ignoramus" and be content. He may accept the advice, or jibe of Mephistopheles and when "knowledge fails may substitute a name." The former plan gives no mental satisfaction and leads to no results. The latter is the plan of the faker when the intent is to make pretence. A third method is to devise an **hypothesis**, that is, make a guess at what may be a correct answer. Thus, when Dalton observed in a few cases the simple integral relation between the varying quantities of one constituent in different compounds of the same component elements, he assumed, *i.e.*, guessed, that the same relation holds in all cases and Berzelius later demonstrated experimentally that the supposition is justified in so many cases that we believe it holds generally, and consequently we have a law of nature; that of **multiple proportions** (*cf.* p. 14).

This sort of hypothesis is not peculiar to science. In all our ways we use it as a guide of action. Examples of the creation and use of such hypotheses range from the most trivial problems to those of great moment. Thus, you may desire to meet a friend. You **suppose** him to be at a certain place. You may test the question by appeal to experiment. Or you may assume that life in a new locality may offer wider opportunities for you. You may test the hypothesis by direct appeal to experiment. Your very presence as a student in college rests upon the **assumption** of benefit. Such hypotheses are continually employed by science and the

scientist, basing his hypotheses on previous experience, is guided by them in his work.

When an hypothesis is such that its assumptions may be tested by **direct** appeal to nature and shown to be correct or incorrect by experiment, Alexander Smith proposes to call it a **stochastic hypothesis** (στοχαστικός = apt to divine truth by conjecture).

**Formulative Hypotheses.** There is, however, another distinct type of hypothesis which we do not expect to test by **direct** appeal to experiment and which is yet capable of giving a degree of mental satisfaction, of serving as a basis of classification of facts, or of serving to suggest methods of study or of experiment. Such hypotheses while they "are pure products of the imagination are the only means by which we extend our knowledge beyond the limits of direct sensation." An example of such hypothesis is the nebular hypothesis of the origin of the starry systems. Whether or not it is correct in its assumptions is a question wholly unanswerable by direct observation or by experiment, but, if correct, these assumptions would entail consequences and these offer problems for the study of astronomers. Such hypotheses may be called **formulative** because they set up a formula, a picture, of what we suppose may be a true state of affairs. If true, the facts we already know must not be out of harmony with them; if useful, they should enable us to say that certain consequences should follow. If an hypothesis is capable of standing these two tests, it is considered more or less valid and may be used for correlation of facts or laws. It is then called a **theory**.

It will be seen that a formulative hypothesis is defined as one not susceptible of direct proof. If a valid hypothesis of this type is called a theory then a theory cannot be proved. It is to be observed, however, that while we recognize two types of hypothesis, we shall find in certain instances considerable difficulty in case we attempt to determine to which class a given hypothesis belongs. Indeed, as times and methods change, pure products of the imagination may become realities and blossoms of past imagination may be fruit in the future. It is always possible then that an hypothesis designed as formulative may evolve into a stochastic one, and its assumptions become facts or laws. It is also to be observed that a formulative hypothesis is a **construction** which is **designed** to fit the facts of science and to serve the purposes of coordination and development. It is, therefore, subject to change, development



and decay. The history of science is strewn with outgrown or outworn theories.

### THE KINETIC-MOLECULAR HYPOTHESIS

At present we have as fundamental hypotheses in chemistry two which serve in a broad sense as the basis of coordination of its facts. These are known as the Kinetic Molecular Hypothesis and the Atomic Hypothesis. It is the chief purpose of this present chapter to show the thought processes by which they were developed, why they were constructed, and, in a preliminary manner, the purposes they serve. Since the chronological order of development is discontinuous and the processes of growth complicated, the discussion will be presented without special reference to time.

We have already considered the law of Boyle, the law of Charles and the law of Gay-Lussac (combining volumes). The questions inevitably arise, why do all gases behave essentially alike when subjected to change of pressure, why alike with reference to volume change with change of temperature, why integral relations when gases unite to form new compounds. The answers seem impossible in terms of fact, but to cry "ignoramus," we do not know, is unsatisfactory as well as resultless. It is obvious, however, that a body of gas, since it occupies a definite space must either fill that space completely or partially. Since, however, all gases are compressible, the simplest conception is, as Hero said (177 B. C.), "There are void spaces between particles of air just as there are between particles of sand; when air is compressed, the particles are forced into the vacant spaces." This may be expressed otherwise by saying: We assume that gases consist of separate particles. These particles are called molecules (from *mol.* = mass and the Latin diminutive). Of course, since any gas may be converted to a liquid and then to a solid and since no matter of any sort is found which does not decrease in volume when subjected to pressure, the assumption may be extended: **All matter is made up of separate particles called molecules.** If, then, on the ground of compressibility of matter, we accept the hypothesis of molecules, it becomes necessary to assume that in gases, the space between the molecules is very large compared with the molecules themselves, since large volumes of gas are compressible to very small volumes of liquid (*cf.* the volume of one gram of water and one gram of

steam, p. 77). If these spaces are relatively very great then it may easily be true that **when gases are compressed the only change which ordinarily occurs is in the space relationship of the molecules** and hence all gases act in general as noted under the heading of Boyle's Law. Again, since all gases increase in volume with the increase of temperature, it may be that **change of temperature simply alters the space relationship of the molecules**. This latter assumption is in accord with the behavior of solids and liquids since they also alter in volume with alteration in temperature.

All gases are characterized by the property of indefinite expansion, the rate of which is expressed by the law of diffusion (p. 61). The additional hypothesis needed to account for this is to assume that **the molecules of gases are not at rest but are in motion (kinetic = motion)**. If the molecules are in motion then it may be that **the pressure of an enclosed body of gas is due to the momentum of the particles striking upon the enclosing surfaces**. Since on standing, a gas neither settles to the bottom of an enclosing vessel nor does any diminution of pressure take place, if our previous assumptions are correct then the **gaseous molecules are perfectly elastic**. It also follows from the fact that the pressure of a given quantity of gas varies inversely as its volume (Boyle's law), that **all the molecules are moving in straight lines**, since if any were moving in circular or other orbits, it would be very probable that an increasing number of orbits would be cut as the volume is decreased by pressure and hence the pressure would increase more rapidly than the concentration. Again, since the pressure of a given quantity of gases increases with increase of temperature at constant volume (Charles' law), it follows that **increase of temperature increases the speed of motion of the molecules**.

Since all liquids are convertible into gases and indeed have at all temperatures a definite vapor tension, we must also assume that **the molecules of liquids are in motion**. In liquids, however, the motion is not free and independent as in gases, but is restricted by the property known as cohesion. The behavior of solids with respect to change of volume when heated or cooled, the vapor tension of certain solids, and the impossibility of determining in all cases whether substances are solid or liquid, make it necessary to assume also that **the molecules of solids are in motion**.

We may now condense our hypothesis: We assume that *all*



*matter is composed of separate particles, called molecules, which are in constant motion, are perfectly elastic, and in gases are wholly independent. In liquids and solids free motion is limited by cohesion. The speed of motion of molecules is changed by change of temperature.* This italicized statement is to be regarded as a "roughed in" hypothesis (the kinetic molecular hypothesis) which presents a picture of what we believe may be a real condition of affairs. The "finishing off" of the picture must await the accumulation of other facts.

It now remains to present a portion of the additional justification for all this fancy, for while, as Tyndall says, "We are gifted with the power of imagination, and by this power we can enlighten the darkness which surrounds the world of the senses," it remains to be seen how such use of it differs from the skill of the maker of fairy tales and how "bounded and conditioned by coherent reason, imagination becomes the mightiest instrument of the physical discoverer."

If our hypothesis be correct, *i.e.*, really represents the facts, we have now a picture not only of what is taking place when gases expand or contract with alteration of pressure and of temperature, but we have also a picture of what takes place when we expose a liquid in an open vessel. Some of the molecules in moving about get beyond the range of cohesive attraction of the other molecules and hence escape and, meeting no permanent obstacle to their progress, continue onward indefinitely, followed by a train of fugitives of more recent escape. The liquid then ceases to evaporate only when it is all vaporized. If, however, we have a closed vessel partially filled with liquid, we may picture the escape of molecules as before; but when they reach the enclosing walls they are turned back, until finally we have as many returning to the liquid surface in a unit time as are escaping from it. We have, then, an equilibrium between the gaseous and liquid form and no further evaporation takes place. Again the motion of the molecules of solids gives us a picture of what takes place when solids go into solution in liquids, and a saturated solution represents that condition where the rates of escape of solute from and into the solvent are equal. When, however, the escape of the solute is more rapid than the process of solution, we may observe such changes as precipitation, crystal formation, etc. The point we seek to emphasize in this paragraph is that by means of this hypothesis we may see that the modes of action of sub-

stances in the gaseous, liquid and solid state are not wholly independent and unlike; and so in the variety of facts, we catch a glimpse of the "interrelatedness of things," one of the objects of science.

**Avogadro's Hypothesis.** — The most important corollary of kinetic-molecular hypothesis is that which was designed to account for the facts represented by Gay-Lussac's law of combining volumes (*q.v.*). This law was announced in 1808. In 1811, Avogadro, an Italian physicist, suggested that in view of these facts it is reasonable to assume that **equal volumes of all gases under like conditions of temperature and pressure contain approximately equal numbers of molecules.** If this hypothesis is correct then the volume ratios of combining gases should be, as they are, expressible by whole numbers. For example, when hydrogen unites with oxygen, if two molecules of hydrogen unite with one of oxygen, then the volume ratio should be two to one. The hypothesis of Avogadro has proved most valuable as a means of correlation of chemical facts and is, indeed, the foundation upon which our present system of correlation rests. However, for the reason that a clear distinction between the molecule as the physical component unit of matter and an equally imaginary chemical unit, the atom, did not formerly obtain, it was not until about 1860 that chemists generally accepted the hypothesis (*cf.* p. 103).

**Molecular Weights.** — The most useful feature of Avogadro's hypothesis grows from the fact that if it is true, we are in possession of a method of ascertaining the relative weights of molecules of gases. If equal volumes contain equal numbers of molecules, then when gases are weighed under like conditions, the weights stand to each other in the same ratio as the weights of the individual molecules. Any series of values showing these weight ratios might be called molecular weights. In the following table are given three series of numbers showing the relative weights of some ordinary gases. The first column gives the names of the gases, the second the weights per liter, the third the specific gravity and the fourth the relative weight using oxygen taken as 32 as a standard of comparison.



Gas.	Weight per liter at 0° and 760 mm.	Specific gravity.	Molecular weight, oxygen = 32
Hydrogen.....	0.0896	0.0696	2.016
Oxygen.....	1.429	1.105	32.0
Water.....	0.8045	0.622	18.016
Air.....	1.293	1.00	28.955
Chlorine.....	3.166	2.449	70.90
Hydrochloric acid.....	1.628	1.259	36.458

These lists might be extended to include all gaseous substances. The series of numbers in the last column are those actually employed under the term, molecular weights. The reason for selecting oxygen with the arbitrarily assumed value 32 as a basis of molecular weights is given on page 102. It is to be observed that were we to measure 32 grams of oxygen at standard conditions, the volume occupied would be 22.4 liters, *i.e.*  $(32 \div 1.429 = 22.394)$ . According to Avogadro's hypothesis, it follows that a molecular weight in grams of any other gaseous substance would occupy a like volume, 22.4 liters. This is known as the **gram molecular volume of gases**. It follows, then, that the **molecular weight of any gas may be found by multiplying the weight of one liter by 22.4**. It is also to be observed that the values in column four of the table may be obtained from those in column three by the proportion  $32 : 1.105 = \text{molecular weight} : \text{specific gravity}$ . The ratio  $32/1.105 = 28.955$ . The value of this observation lies in the fact that physicists usually record their determinations of weight relations of gases in terms of specific gravities (air = 1) and tables of these values are available for the use of chemists. We may then obtain the molecular weight of any gas by multiplying its specific gravity by 28.955. The quantity, 28.955 is, of course, the average of the molecular weights of the components of the air.

#### THE ATOMIC HYPOTHESIS

In 1803, an English chemist, John Dalton (see Heroes of Science, Chemists) converted the ancient atomic hypothesis into an important factor in the development of chemistry. The origin of the hypothesis probably dates back to the very beginnings of Hindu philosophy. The early Greek philosophers considered that *all matter consists of discrete particles which are indivisible*. These atoms (from  $\alpha = \text{not}$ , and  $\tau\acute{\epsilon}\mu\eta\nu\epsilon\iota\nu = \text{to cut}$ ) were assumed to be in

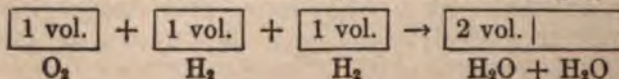
constant motion and separated from each other by void spaces. Dalton, to whom we more or less clearly owe the law of multiple proportions and to whom the laws of conservation of mass and of definite proportions were known, sought an answer to the query; why do the facts summarized by these laws exist? While not historically exact, we may assume that he reasoned somewhat as follows: If the atomic hypothesis is correct and atoms are indivisible; if we further assume that *chemical reaction takes place between atoms* and that *all atoms of one substance are like in weight* and that *atoms of unlike substances differ in weight*, then the laws of conservation of mass, definite proportions and multiple proportions should exist. Thus, if atoms are indivisible, no change can be considered as sufficiently drastic to effect the destruction of matter. Again, if chemical change takes place between atoms, it should be true, as it is, that when chemical change takes place between unlike atoms, the weight ratio is constant, since a given quantity of the substance produced represents the weight of a definite number of atoms of each constituent. Similarly, it follows that if more than one compound is made from the same materials, the variation in weight can only be in multiples of the weight of single atoms. It is true that a study of Dalton's own work shows no adequate foundation of experimental fact for this sweeping hypothesis nor indeed for the law of multiple proportions itself (cf. p. 15). It was fortunate that the great Swedish chemist, Berzelius, was much impressed by Dalton's work and amply confirmed by experiment the latter's conclusions regarding the law of multiple proportions and, to a very great extent, justified the assumptions of the hypothesis. The fundamental points of the atomic hypothesis as presented by Dalton are those italicized above. The present-day atomic conception differs materially from that of Dalton (cf. Structure of the Atom, Chap. XXXIII), but it is important to note that it was these views of Dalton which largely controlled the trend of chemical nomenclature.

**Atomic Weights.** — The first and most obvious consequence of Dalton's views was that it seemed possible to determine the **relative weights** of the atoms by determining the proportions by weight in which the elements combine. This problem Dalton, and more especially Berzelius, attempted to solve. The methods employed were essentially those described on p. 16 *et seq.* for determination of equivalent weights. Two difficulties presented themselves.



The first was the selection of a unit of measure. Since any element might be selected and arbitrarily assigned an atomic weight, this difficulty might seem only a minor one. If, however, atomic weights are to be used as units of measure, a general agreement is essential. It is impossible here to discuss the details of the long story of the selection of a unit of measure. It is sufficient to say that in 1905 an international committee, consisting of representatives of the chemical societies of the world, agreed upon oxygen with an assigned atomic weight of 16 as the most convenient standard of measure of atomic weights. The second difficulty encountered may be illustrated as follows: Black copper oxide consists of 79.9 per cent of copper and 20.1 per cent of oxygen. If the combination is in ratio of one atom of copper and one of oxygen, then the atomic weight of copper is 63.6 ( $20.1 : 79.9 = 16 : 63.6$ ). But red copper oxide consists of 88.83 per cent of copper and 11.17 per cent of oxygen and therefore since  $11.17 : 88.83 = 16 : 127.2$ , the atomic weight may be 127.2. If we adopt the number 63.6, the formulae of the two oxides are: black oxide,  $\text{CuO}$ , red oxide,  $\text{Cu}_2\text{O}$ . If we choose the atomic weight 127.2, the black oxide becomes  $\text{CuO}_2$ , the red oxide,  $\text{CuO}$ . The attempt to select atomic weights meets a like difficulty with many elements. Berzelius adopted certain arbitrary rules as a guide and succeeded in developing a table of atomic weights marvelously like those in present use. There was, however, no general agreement among chemists with respect to these weights until after Cannizzaro, in 1858, suggested that the hypothesis of Avogadro might be used as a final criterion. (Alembic Club reprints No. 18.) It is probable that such use of Avogadro's hypothesis would have been made much earlier if a clear distinction between the atoms of elements and molecules had obtained. The failure to recognize this distinction precluded the possibility of the acceptance of the hypothesis.

Gay-Lussac had shown (cf. p. 74) that two volumes of water vapor are produced from two volumes of hydrogen and one of oxygen. If no difference exists between atoms and molecules, then Avogadro's hypothesis is false since for each molecule of oxygen we get two of water and each of the latter is partly oxygen. If, however, we assume hydrogen and oxygen molecules to be diatomic, the hypothesis may be valid. This may be illustrated in graphic form.



While these ideas seem to have been clear to Avogadro in 1811, it was not until the publication of Cannizzaro's paper (1858) that chemists generally recognized the validity of Avogadro's hypothesis and were prepared to accept his definition: "A molecule is the smallest particle of an element or compound which exists free in a gas." Cannizzaro proposed to use this definition of a molecule as a starting point and since the relative weights of gases are molecular weights, to select as the atomic weight of an element the least amount of that element present in a gram molecular weight of any of its volatile compounds. The choice of atomic weights becomes, therefore, a matter of laboratory determination.

**Selection of Atomic Weights.**—We have now the atomic weight of oxygen arbitrarily selected as 16. We have also a basis of selection of the atomic weights of other elements. If it were desired to find the atomic weight of hydrogen, we could proceed as follows: We select a volatile compound of hydrogen and determine its molecular weight. Water is a volatile hydrogen compound with a specific gravity as a gas of 0.622. Its molecular weight is therefore approximately 18 (*cf.* exact molecular weights, p. 105). Careful analysis of water shows its composition (*cf.* p. 74) to be 16 parts by weight of oxygen to 2.016 parts of hydrogen. The atomic weight of hydrogen may be 2.016. If, however, we proceed to ascertain the molecular weights and the composition of gram molecular weights of a number of other hydrogen compounds, we obtain a series of results as indicated in the following table:

Compound.	Molecular weight.	Hydrogen.	Other elements.	
Water.....	18.016	2.016	Oxygen.....	16
Hydrogen peroxide....	34.016	2.016	Oxygen.....	32
Hydrochloric acid.....	36.468	1.008	Chlorine.....	35.46
Ammonia.....	17.064	3.024	Nitrogen.....	14.04
Hydrogen sulfide.....	34.076	2.016	Sulfur.....	32.06
Methane.....	16.032	4.032	Carbon.....	12.0

The number, 1.008, represents the smallest quantity of hydrogen which appears in a gram molecular weight of any of these compounds. It may, therefore, be used as the atomic weight of hydrogen unless some compound were discovered in which a gram molec-



ular weight should contain less than 1.008 grams of hydrogen. No such compound is known. Having found that no smaller weight than 1.008 need be used to represent the combining weight of hydrogen, we may apply the same method successively to all other elements. If the numbers, 35.46, 14.04, 32.06 and 12.0 represent the atomic weights of chlorine, nitrogen, sulfur and carbon, the formulas of the compounds in the above table are water,  $\text{H}_2\text{O}$ , hydrogen peroxide,  $\text{H}_2\text{O}_2$ , hydrochloric acid,  $\text{HCl}$ , ammonia,  $\text{NH}_3$ , hydrogen sulfide,  $\text{H}_2\text{S}$  and methane,  $\text{CH}_4$ .

Another example may be given for the sake of emphasizing the fact that analysis alone is not sufficient to establish atomic weights. Let us suppose we have established the fact that the atomic weight of chlorine is 35.46. There is a compound of phosphorus and chlorine, the analysis of which shows it to consist of 35.46 parts chlorine to 10.33 parts phosphorus. The chloride of phosphorus in question has a molecular weight of 137.46. The quantity of phosphorus in a gram molecular weight is therefore 31 grams. Since no compound of phosphorous is known which contains a less amount per gram molecular weight, 31 is, therefore, the atomic weight and not 10.33. For supplementary methods of obtaining atomic weights, the student is referred to p. 108 and to text-books on physical chemistry.

**Exact Atomic Weights.**—So far in the discussion of atomic weights, we have assumed that exact values of the atomic weights may be obtained by analysis of gram molecular volumes of gaseous substances. For various reasons the values thus obtained are not so exact as those gotten by indirect methods. For example, assuming the atomic weight of silver to be known, the atomic weight of chlorine may be more accurately ascertained by analyzing silver chloride than by attempting to determine the weight of chlorine in 22.4 liters of gaseous hydrochloric acid. Very accurate analysis of this sort is known as atomic weight determination. An enormous amount of painstaking labor has been expended upon this problem. Even with the utmost care and with the use of the most refined instruments, these measurements are subject to small errors which are due to imperfections of apparatus, impurities of reagents and other causes some of which may be unknown to the analyst. For example, the classic research of Dumas on the composition of water (p. 72) was vitiated by a cause by him, wholly unsuspected, the occlusion of small amounts of

hydrogen by copper. Such errors are what is known collectively as experimental error and are the reason that different analysts secure slightly varying results. A consequence of these errors is that from time to time the atomic weights must be readjusted to conform with the most reliable measurements available. To facilitate this readjustment, an international committee is appointed to review the work on atomic weights and publish annually a list which is known as the international atomic weights. These weights are used whenever calculations involving chemical relations are required. It is not to be understood that the actual atomic weights vary from year to year. It is the accuracy with which they have been determined which varies.

**Exact Molecular Weights.** — The molecular weight of oxygen is exactly thirty-two. The reason for adopting this number is clear since if sixteen is arbitrarily chosen as the atomic weight of oxygen and the element is diatomic (*cf.* p. 102) the molecular weight is also arbitrarily selected. The gram molecular volume of oxygen is then 22.4 liters. So far in the previous discussion of molecular and atomic weights, it has been assumed that 22.4 liters is the exact volume of a gram molecular weight of all gases. This is not strictly true. It would be true probably if all gases conformed strictly with the generalizations of Boyle, Charles and Gay-Lussac. They do not do so for reasons which are wholly in accord with the kinetic molecular hypothesis. A full discussion of these reasons is properly a part of physical chemistry and is usually presented in connection with Van der Waal's equation (see text-books on Physical Chemistry). Direct determination of the weight of 22.4 liters of gaseous substances at 0° and 760 mm. does not give the **exact** but only the approximate molecular weights. The analytical results obtained in determining the composition of substances are, however, subject to variations by no means so great as those obtained by the weighing of gases. For example, the weight of 22.4 liters of hydrogen is 2.012 grams. The atomic weight of hydrogen is 1.008 and since hydrogen is diatomic (p. 100) its exact molecular weight is 2.016. The following table will illustrate the magnitude of the variations between observed and exact values (*cf.* also p. 118).



Gas.	Density.	Observed molecular weight.	Exact molecular weight.
Hydrogen.....	0.0695	2.012	2.016
Oxygen.....	1.105	32	32
Chlorine.....	2.490	72.01	70.92
Carbon dioxide.....	1.529	44.27	44.00
Ammonia.....	0.597	17.26	17.06
Sulfur dioxide.....	2.264	65.54	64.06
Phosphine.....	1.214	35.15	34.06
Hydrochloric acid.....	1.269	36.72	36.468
Hydrogen sulfide.....	1.189	34.43	34.076
Nitrogen.....	0.967	28.07	28.08
Nitric oxide.....	1.0387	30.07	30.01

**Valence.**— Referring to the table on p. 103, it may be seen that one atomic weight of chlorine, oxygen, nitrogen and carbon unite respectively with one, two, three or four atomic weights of hydrogen. It will be seen, then, that if we are to use atomic weights as units for the expression of chemical composition, the atomic weights of different elements are not necessarily of equal value. If we use hydrogen as a basis of comparison, we see that the numerical combining values of atomic weights of these four elements are in the ratio of 1 : 2 : 3 : 4. This numerical value of atomic weights of the elements in terms of hydrogen is known as *valence* (*cf.* also p. 65).

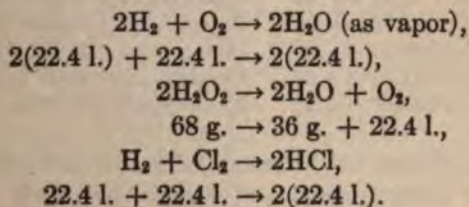
We have already noted the fact that the valence of an element may be variable (*cf.* p. 102). We shall find, as we proceed, that this variation depends upon the character of the elements and the conditions of reaction. It is sufficiently regular to be very serviceable in the study of chemical relations. The relation of atomic to equivalent weights is now clear. The atomic weight of an element is equal to the equivalent weight multiplied by the valence. When an element manifests more than one equivalent weight, its valence is correspondingly variable (*cf.* Chapter XXXVI).

**The Reality of Atomic and Molecular Weights.**— The student is urged to keep in mind that atoms and molecules are **imaginary quantities** and may or may not have a real existence. It is true also that recent investigations have rendered the actual existence of both molecules and atoms so extremely probable that few scientists doubt their real existence, yet the development of

these concepts was a pure product of the imagination. On the other hand, the student must clearly understand that molecular weights and atomic weights are real. Molecular weights are the relative weights of equal quantities of gases compared with oxygen with an assigned value of 32. Atomic weights are the weight units in which we express the composition of compounds and moreover express in grams the smallest quantity of each element occurring in a gram molecular volume of any of its volatile compounds.

**Molecular Formulas and Equations.** — A very valuable extension of the use of formulas and equations is now possible. We may use formulas not only to represent the composition of the compounds, but we may, by means of formulas, represent the molecular weights of elements and compounds. The molecular complexity of elements is indicated by subscripts appended to the symbols. Thus the table on p. 106 indicates that the formulæ of oxygen, hydrogen, nitrogen and chlorine are  $O_2$ ,  $H_2$ ,  $N_2$  and  $Cl_2$ , respectively. Certain elements are more complex, thus the formula of phosphorus vapor is  $P_4$ ; of sulfur  $S_8$ . Some elements are mon-atomic, e.g., argon, A; zinc vapor, Zn, etc.

If we use molecular formulas to represent chemical changes and the molecular formulas of the products are likewise indicated, we have what are known as molecular equations. Such equations not only convey the expression of molecular quantities but, if the reacting materials are gaseous, the volume relations are also indicated. In subsequent chapters, whenever possible, equations will be expressed in molecular form. A few illustrative examples are cited.



**Additional Methods of Determining Molecular Weights and Atomic Weights.** — As the student further pursues the subject, he will encounter various means by which molecular weights are determined besides the fundamental one of the relative weights of gases. Of these, the more important are the freezing point,



boiling point and osmotic pressure methods later detailed in Chapter IX. There are several methods, such as the method of co-volumes, the analysis of salts, the rates of diffusion of gases, etc., not discussed in this text. For a discussion of these, the student is referred to texts on physical chemistry. These methods serve not only as checks upon the accuracy of the fundamental method but also serve to extend our knowledge of molecular weights to substances not obtainable in the gaseous condition. For example, hydrogen peroxide (*cf.* p. 103) cannot be obtained as a gas, but the freezing point method (*cf.* p. 162) shows its molecular weight to be 34 and its formula is consequently  $\text{H}_2\text{O}_2$ .

We have also a variety of methods of checking the atomic weights selected as those representing the smallest weights of the various elements present in gram molecular volumes of their volatile compounds. One of these, the **Law of Dulong and Petit**, is particularly valuable, since it not only checks the fundamental methods where both are practicable, but serve as a means of ascertaining atomic weights of certain elements which have no volatile compounds. The law was announced in 1818 as a result of the observation of Dulong and Petit that the specific heat of the elements in the solid state multiplied by their atomic weights gives an approximate constant which is in the neighborhood of 6.4. This rule is not a rigid one, as is shown by the following table, and for that reason is sometimes called Dulong and Petit's approximation.

Element.	Sp. ht.	At. wt.	C.	Element.	Sp. ht.	At. wt.	C.
Lithium..	$0.9408 \times$	$6.94 =$	6.53	Cadmium.....	$0.0514 \times$	$112.4 =$	5.78
Silver....	$0.0559 \times$	$107.88 =$	6.03	Lead.....	$0.03096 \times$	$207.1 =$	5.78
Gold.....	$0.0304 \times$	$197.2 =$	6.25	Iron.....	$0.1098 \times$	$55.5 =$	6.12
Copper...	$0.0923 \times$	$63.57 =$	5.88	Uranium.....	$0.0277 \times$	$238.5 =$	6.61
Bismuth..	$0.0305 \times$	$208.00 =$	6.34	Mercury (solid)	$0.0335 \times$	$200.0 =$	6.7

The values shown lie between 5.78 and 6.7. If a few elements, such as silicon, boron and carbon, had been included the product of the specific heat at, or near, the ordinary temperature times the atomic weight would be for these elements 4.8, 2.6 and 2.35; but if the specific heat were measured at higher temperatures the value of the product approaches more nearly 6.4, *e.g.*, carbon at  $977^\circ$  has a specific heat of 0.467, which gives as a "constant" 5.8. The variations from a constant are probably due in part

to the fact that the specific heat values are not taken under comparable conditions and in part to the differences in the molecular complexity of the elements. It would lead too far to enter into a detailed discussion of these variations. It is sufficient for our present purpose to say that in spite of these variations the rule is sufficiently exact to enable us to choose between various equivalent weights, found by analysis, in selecting an atomic weight. Thus, if an element were to be discovered and on analysis shown to have, as an oxide, an equivalent weight of 117, but with a specific heat such that  $\text{sp. ht.} \times 117 = \text{approximately } 3.2$ , we should at once conclude that the atomic weight is probably 234, whether volatile compounds could be prepared or not. In general, then,  $6.4 \div \text{sp. ht.} = \text{the approximate atomic weight}$ .

There are several other methods, available in special cases, for determining atomic weight values. It is necessary to mention here only the Periodic Law (*q.v.*), the Law of Isomorphism (*q.v.*) and the ratio of specific heat of gases at constant pressure to that at constant volume (p. 278). These will be further discussed subsequently.

**Exercises.** — 1. In what sense may a stochastic hypothesis be "proved"?

2. First make a clear statement of the essential features of the kinetic molecular hypothesis, and then show how it "explains" the laws of Boyle and Charles and the law of diffusion.

3. Show how the kinetic molecular hypothesis explains the vapor tension of liquids and the "flow" of such substances as sealing wax, glass, glaciers, etc.

4. The specific gravity of certain gaseous compounds referred to air is as follows: *A*, 2.263; *B*, 6.86; *C*, 1.189; *D*, 1.1529. What are the corresponding weights per liter and molecular weights?

5. A substance at 760 mm. and 0° C. weighs 1.9768 grams per liter. On analysis it is found to consist of exactly 72.72 per cent oxygen and 27.28 per cent carbon. What is the "observed," and what the "exact" molecular weight?

6. State in outline the essential features of Dalton's atomic hypothesis and then show in detail how it explains the laws of definite and multiple proportions.

7. A certain element has only one known volatile compound with a specific gravity, 12.85. It consists of 38.11 per cent chlo-



rine and 61.89 per cent of the other element. What is the molecular weight of the compound and the atomic weight and the valence of the element?

8. The molecular weight of a certain substance is 52.08. It consists of 46.08 per cent carbon and 53.92 per cent nitrogen. What is the molecular formula of the substance? (See table for atomic weights of carbon and nitrogen.)

9. If Avogadro's hypothesis is accepted as true and the volume relations of nitrogen and hydrogen in uniting to form ammonia are, 1 vol. of nitrogen and 3 vol. of hydrogen give two volumes of ammonia ( $\text{NH}_3$ ), what is the molecular formula of nitrogen?

10. If 1 vol. of phosphorus vapor and 6 vol. of chlorine unite to form four volumes of phosphorus trichloride, what is the molecular formula of phosphorus? (The atomic complexity of chlorine is shown by the formula  $\text{Cl}_2$ .)

11. A new substance has a specific gravity of 11.8 as a gas. Its composition is 30 per cent of a new element and 70 per cent bromine. What are the approximate and the exact molecular weights of the new substance and the atomic weight and the valence of the new element?

12. In terms of kinetic molecular hypothesis, how do you explain the difference between ice and water?

Explain the equilibrium between water and its vapor. How does temperature affect equilibrium? (Answer this question from the viewpoint of the hypothesis.)

13. What would be the value of the G.M.V. at  $100^\circ$  and 1000 mm.?

14. The density of a gas compared to oxygen is 0.9756. What is its molecular weight?

15. The density of a gas referred to air is 0.8507, what is its molecular weight? What is the weight of 1 liter of the gas?

16. Upon what evidence are we justified in making the assumption that the chlorine molecule is 2.28 times as heavy as the oxygen molecule? Give a list of the facts and assumptions which underlie this assumption.

17. (a) Suppose that mercuric chloride, phosphorus trichloride and phosphorus oxychloride were the only volatile compounds of chlorine known, the weights of chlorine contained in the G.M.V. being 70.9, 106.35 and 106.35 grams respectively for each of the compounds, what would be the value of the atomic weight of the chlorine?

(b) If the weights of chlorine in the G.M.V. of three volatile chlorides were 70.9, 141.8, 212.7 grams, what would be the value for the atomic weight of chlorine based on these data?

18. The weights of a new element X contained in the G.M.V. of its known volatile compounds were respectively 145 and 290 grams. What is its atomic weight?

If a hydride of X were discovered which possessed the molecular weight 73.6, how would the value of the atomic weight be modified? What is the valence of X?

19. What numerical relationship obtains between the atomic and equivalent weights of an element? Between the molecular and atomic weights? Hence, what relationship holds between molecular and equivalent weights? What facts must be known in order to establish the atomic weight of copper?

20. An oxide of sulfur contains 50 per cent of sulfur and 50 per cent of oxygen. If its molecular weight is 128, what is its molecular formula?

21. What weight of sulfur would be required to produce 10 liters of sulfur dioxide at  $10^{\circ}$  and 780 mm.? What volume of oxygen would be required? Employ the method of molecular equations.

22. What volume of carbon dioxide at  $400^{\circ}$  is produced by heating 1 kg. of limestone to  $812^{\circ}$ ?

23. What are the volume changes involved in the following interactions, it being assumed that pressure remains constant and that the temperature of the interacting substances is the same as that of the products: (1) union of hydrogen and bromine, (2) union of hydrogen and oxygen, (3)  $2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2$ , when the decomposition is half complete?

24. Give molecular equations for: the displacement of hydrogen from an acid by aluminium, the displacement of hydrogen from sodium hydroxide by zinc, the action of chlorine on water, the interaction of potassium permanganate and hydrochloric acid, the action of steam on red hot iron.

25. The specific heat of an element is 0.063 and its equivalent weight ( $\text{O} = 8$ ) is 34.3. What is the atomic weight?

26. Write the equations in molecular form, for the decomposition by heat of  $\text{KClO}_3$ ;  $\text{BaO}_2$ ;  $\text{MnO}_2$  and  $\text{KNO}_3$ , and then calculate from these the volumes of oxygen produced by heating 20 grams of each.



27. In the preparation of hydrogen and oxygen from water by electrolysis, what volume of each is produced from 54 grams of water.

28. How many liters of hydrogen are obtained by treating 27 grams of aluminium with hydrochloric acid? (Write the molecular equation and obtain answer from that.)

## CHAPTER VI

### CHLORINE AND HYDROGEN CHLORIDE

**Occurrence.** — Chlorine does not occur free in nature. Sea water contains large quantities of its compounds. Analysis of sea water shows it to contain about 3.6 per cent of solids of which the chief compounds are: salt,  $\text{NaCl}$ , 77 per cent, magnesium chloride,  $\text{MgCl}_2$ , 8.8 per cent, potassium chloride,  $\text{KCl}$ , 2.5 per cent. Great deposits of salts, probably formed by evaporation of sea water, are found in various parts of the world. Ordinarily, the deposits are in more or less sharply defined layers formed by the process of fractional crystallization. The greatest deposits are found in Europe along a line running approximately from the mouth of the Rhine to the mouth of the Danube. These deposits have, in some cases, been worked for common salt for hundreds of years. The most famous mines are probably those at Stassfurt. These are notable not only as salt mines but also as sources of potassium and magnesium salts and of bromine (*q.v.*). A similar series of salt deposits is found in the region of western New York, southern Michigan, Ohio, West Virginia and Kentucky.

Many inland lakes, such as the Caspian Sea, the Dead Sea, Great Salt Lake, etc., also are rich in chlorides. Extinct lakes such as these are supposed to be the source of such deposits as those of Oklahoma and Kansas. Compounds containing chlorine, chiefly common salt, are found in all soils, and hence are also present in all surface or sub-surface waters, usually in small quantities. The animal organism also contains chlorine compounds. The gastric juice contains about 0.1 per cent of hydrogen chloride and the blood contains calcium chloride, potassium chloride and common salt in about the same relative proportions in which they are found in sea water though only one-third as concentrated. All herbivorous animals have a normal craving for sodium chloride which must be satisfied if health is maintained.

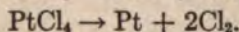
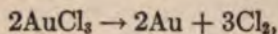
**History.** — Although chlorine compounds, especially salt, have been known and used by man from prehistoric times and "salt"



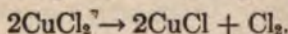
was one of the alchemistic "elements," the recognition of chlorine as a constituent factor was accomplished only in 1774 by Scheele, who called it "dephlogisticated muriatic acid," since he prepared it by treating hydrochloric acid (muriatic acid) with manganese dioxide, the product being capable of supporting combustion. Lavoisier (1789), on the assumption that all acids contain oxygen, called the gas oxymuriatic acid, and assumed the relation between hydrochloric acid and chlorine to be the same as between sulfurous and sulfuric acids (*q.v.*). Gay-Lussac (1809) endeavored in vain to reduce this supposed oxide and in 1810 Sir Humphrey Davy in an exhaustive research (see *Alembic Club reprints No. 9*) showed that so far as was then known there was no satisfactory evidence of the substance being complex, and he proposed to consider it an element and to call it chlorine ( $\chi\lambda\acute{o}\rho\omicron\varsigma$  = greenish yellow) because of its color. This view obtains at present and, following the example of Davy, several subsequently discovered elements have been named from some striking physical property. (See bromine, iodine, etc.)

**Preparation.** — The methods of preparing chlorine will be considered under three heads:

1. **By Heating Chlorine Compounds.** — Many chlorides when heated are decomposed and one of the products is chlorine; thus platinic chloride and gold chloride decompose readily at moderate temperatures, as indicated:

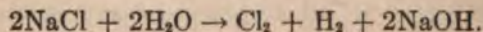


While cupric chloride gives on heating the cuprous compound:



Unfortunately for the application of the process, the naturally occurring chlorides decompose only at such high temperatures as to render the method impractical; thus sodium chloride is not decomposed at its boiling temperature of 1750° C.

2. **Electrolytic Methods.** — If a solution of common salt or of hydrochloric acid be electrolyzed chlorine appears at the positive pole (the anode) and sodium, or hydrogen, at the negative pole (the cathode). In the case of the electrolysis of sodium chloride, the sodium reacts with water and gives sodium hydroxide, so that the net result is



If the process is to be carried out on a practical basis, the electrodes must be separated to prevent the interaction of the products by mixing through diffusion. This mixing is prevented either by means of a membrane of earthenware, asbestos, Portland cement, etc., or by placing the anode in a separate compartment (the Bell process); or by using mercury as a cathode (Fig. 32). In the last case the sodium unites with the mercury to form an amalgam which may be removed from time to time and washed with water to obtain sodium hydroxide (Castner's Process). Fused chlorides are also electrolyzed and various devices are employed to keep the products separate. For full details the student is referred to Thompson's Electrochemistry.

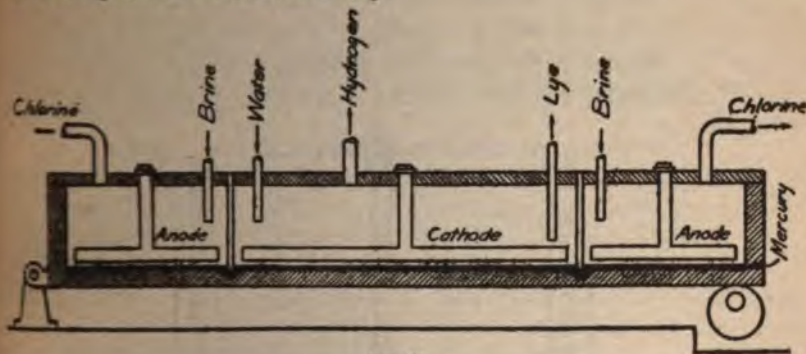
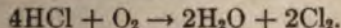
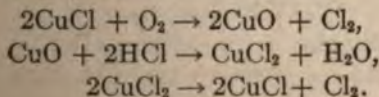


FIG. 32.

**3. Oxidation of Compounds of Chlorine.**—Oxidation of hydrochloric acid by air is not possible by direct action, *i.e.*, by simple burning of the acid. But by the use of a catalytic agent and the principle of mass action (*q.v.*) this result may be reached (Fig. 33). Hydrogen chloride mixed with air is passed through a tube heated to about  $400^{\circ}$  and containing pumice stone which has been treated with a solution of copper chloride. The result of the reaction is



If cuprous chloride be used, it remains in the same condition at the end as at the beginning of the reaction. It does *not* follow that it remained the same *during* the reaction. The following changes probably take place:





The chlorine so obtained is contaminated with unburned hydrochloric acid, water, unused oxygen, and nitrogen from the air. The acid can, of course, be removed by washing with water and the impure chlorine used in processes where the impurities are of little or no consequence, *e.g.*, in the manufacture of bleaching powder (*q.v.*). This process is of commercial application and is known as Deacon's process.

The same result, oxidation of hydrochloric acid, may be accomplished more readily, though not more cheaply, by using hydrochloric acid in solution in water and any fairly active oxidizing agent. A few examples and the equations are given:

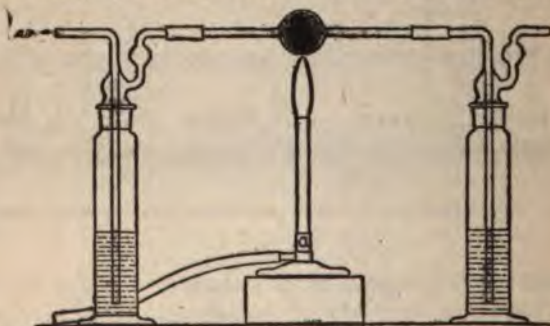
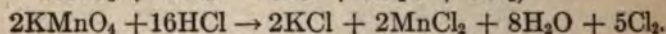
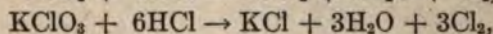
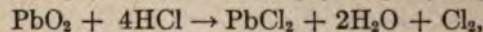
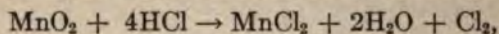
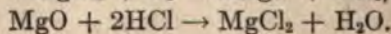
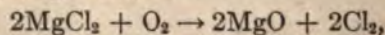
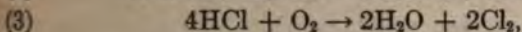
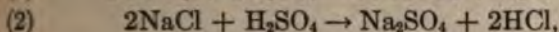
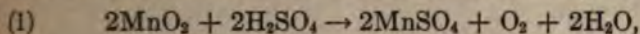


FIG. 33.

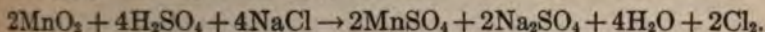
The first reaction is especially interesting because, by the Weldon recovery process, the manganese chloride can be converted into an again available substance, as follows: If mixed with milk of lime ( $\text{Ca}(\text{OH})_2$ ) in suspension and air is blown through the hot mixture it is converted into a substance known as calcium manganite, which may be regarded as  $\text{CaO} \cdot \text{MnO}_2$ . This is insoluble and settles out as a "mud," which may then be used as before. In 1885, Weldon and Pechiney suggested the heating of magnesium chloride,  $\text{MgCl}_2$ , in a current of air and then treating the oxide with hydrogen chloride:



The process is therefore continuous and is very satisfactory. It is also possible to manufacture the hydrochloric acid and oxidize it in one operation. This is the most common laboratory process. Salt and sulfuric acid are mixed and the reactions may be expressed:



or by adding the three equations (multiplying (2) by the factor 2 to supply the required acid), we have:



Of these methods the electrolytic seem destined to become the commercial processes though, because of convenience of laboratory manipulation, the oxidation processes will probably remain as the laboratory method.

#### *Physical Properties. —*

Specific gravity, 2.49.

Weight of 1 l., 3.220 g.

Solubility in water:

At 0° 461 vol. in 100.

At 20° C. 215 vol. in 100.

Critical temperature, 146° C.

Boiling point, -33.6° C.

Specific gravity of liquid, 1.47.

Melting point, -102° C.

Vapor tension at 0° = 3.66 At.

Molecular weight, 72.2.

At. wt., 35.46.

Chlorine may very readily be collected by displacement of air, since it is so much heavier than air (ratio 2.49 : 1). For this purpose it is delivered into the bottom of the vessel and the air is displaced upward. On account of the relatively high density of both gases the rate of diffusion is slow and hence there is not sufficient diffusion to materially dilute the chlorine if the rate of preparation be fairly rapid. The gas may not be collected conveniently over mercury because it attacks the latter. If collected over water the loss of gas is considerable because of its solubility. It may, however, be collected over saturated salt solution, in which it is much less soluble than in water. As a gas it is greenish yellow in color. Its odor is characteristic and unpleasant and the effect on the nasal membranes irritating. Inhalation of considerable quantities may produce fatal effects.

The solution of chlorine in water is of the same color, odor and taste as the gas itself. If chlorine be passed into water at



0° C., yellow octohedral crystals of chlorine hydrate,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , are formed, which decompose spontaneously, even at 0°, when exposed to the air because of the high vapor tension. At 10° the vapor tension is 832 mm. This substance is of special interest because, using it, Faraday, in 1823, liquefied chlorine, thus initiating a series of experiments which have ultimately resulted in the liquefaction of all gases and the demonstration that the solid, liquid and gaseous states are not inherent properties of substances, but a function of the temperature. The simple experiment of Faraday also illustrates the principles which have since proved uniformly effective. Faraday sealed some chlorine hydrate in a bent tube. The end containing the hydrate was placed in warm water, while the other was immersed in a mixture of ice and salt. (See Fig. 34.)

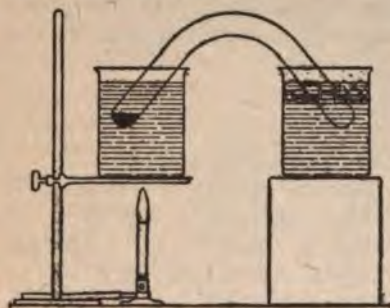


FIG. 34.

It will be observed that by thus increasing the pressure and lowering the temperature the gas becomes condensed to liquid form. This treatment is sufficient to liquefy any gas, provided the lowering of the temperature be sufficient to bring the gas below the critical temperature. In terms of the kinetic molecular hypothesis, the explanation is that by lowering the temperature of any gas the

rate of motion of the molecules is decreased and hence the violence of their impacts lessens and consequently, if kept at a constant pressure, the molecules are brought closer together.

When either by lowering the temperature or by increase of pressure, the molecules are approached sufficiently close to each other so that cohesion, whatever that is, becomes effective, we have liquefaction. It will be seen that, however closely gas particles are brought together, if their rate of motion is very great the violence of impact against each other prevents cohesion. Hence for every gas there is a temperature, called the critical temperature, to which it is necessary to cool a gas so that with sufficient pressure, the critical pressure, it will liquefy. This is found to be, as we have noted, -118° for oxygen; -231° for hydrogen; 374° for water and 146° for chlorine. If a gas is above the critical temperature no pressure is apparently sufficient to

cause liquefaction, even though the concentration, *i.e.*, the specific gravity, be made greater than that of the liquid. In terms of the hypothesis, again the rate of motion, a function of the temperature, is so great that the molecules may not cohere to the degree characteristic of the liquid state. The student should carefully distinguish between fact and fiction in the foregoing statements.

In the table of physical properties the molecular weight is given as 72.2, while twice the atomic weight would call for an adjusted molecular weight of 70.92. The explanation of the discrepancy is found in terms of the kinetic hypothesis as follows: 22.4 l. of chlorine at 0° and 760 mm. pressure weigh 72.2 grams, while if chlorine "obeyed" Boyle's and Charles' law perfectly the weight should be 70.92 grams. That is, 22.4 l. of chlorine contain more molecules than 22.4 l. of oxygen under the same conditions. Such should be the case did the molecules of chlorine exert an appreciable attraction for each other. That they do so with sufficient increase of concentration is shown by liquefaction at sufficient pressure. The principle of continuity would not lead us to expect an abrupt cessation of this attractive effect as the pressure becomes less. We, therefore, still use the general statement of Avogadro with the modification that all gases are of *approximately* equal molecular concentration under like conditions, particularly since it is possible to account for and indeed calculate the variations by use of van der Waal's equation (see texts on Physical Chemistry).

**Chemical Properties of Chlorine.** — The chemical behavior of chlorine may be conveniently considered under two heads.

1. **Direct Union with Elements and Compounds.** — We have already considered indirectly the union of chlorine with water to form chlorine hydrate,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ . This union takes place at 0° and the compound is unstable at and above that temperature. Since in terms of the valence hypothesis we ordinarily consider oxygen as bivalent and hydrogen as univalent, we have in water a compound which is saturated and so content ourselves with not attempting to express the valence relation between the chlorine and the water in this, as well as in other hydrates.

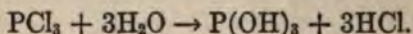
With carbon monoxide, chlorine, in the sunlight, unites to form an easily liquefiable gas called phosgene,  $\text{COCl}_2$  (b. p. 8° C.). This substance has played a considerable part in the development of organic chemistry.

With other elements chlorine unites with varying ease to form



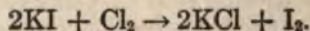
chlorides. The most important of these is hydrogen chloride, which in solution is known as hydrochloric acid (*q.v.*).

If chlorine be heated with phosphorus, sulfur, sodium, potassium, etc., chlorides are formed and the physical phenomena of heat and light accompanying the reaction are very similar to those observed with oxygen. Hence we say these substances burn in chlorine. With certain other elements, such as oxygen, carbon, nitrogen, etc., chlorine will not unite directly by heating the substances together, but by indirect methods the chlorides may be prepared and are of varying, though usually slight, stability. Some of these will be considered shortly. Chlorides, however formed, may be considered as of two types, those which are decomposed by water, furnishing hydrochloric acid and the acid of the other element, and those not so affected. An example of the first type is furnished by phosphorus trichloride, which reacts with water according to the equation:

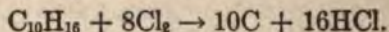


This sort of reaction is known as hydrolysis and will be more fully discussed later (p. 182). The speed and extent of such decompositions vary with the chloride employed. There is another distinct type of chloride in which no appreciable double decomposition of this character occurs. An example is furnished by common salt, NaCl. The behavior of phosphorus trichloride and water is characteristic of a class called non-metallic chlorides, while chlorides which act in water as does common salt are known as metallic chlorides. There are individual chlorides, of course, which react so slowly or so slightly with water as to render their classification as metallic or non-metallic doubtful.

**2. Substitution and Displacement.**—Chlorine also is able to displace other elements from compounds. This mode of behavior is of great importance because of both its practical and scientific value. If, for example, chlorine is passed into a solution of potassium iodide we obtain potassium chloride and iodine.

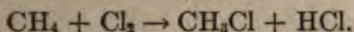


Another example is furnished by turpentine,  $\text{C}_{10}\text{H}_{16}$ , which, if warmed, reacts violently as indicated:

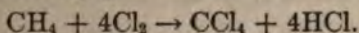


Very frequently, especially with hydrogen compounds, the displacement by chlorine may be regulated so that it will take place

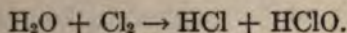
in stages such that the result is two compounds containing chlorine, *e.g.*,



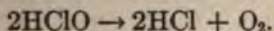
The reaction takes place slowly in the sunlight, but if continued sufficiently will ultimately give carbon tetrachloride,  $\text{CCl}_4$ .



This kind of displacement by chlorine is sometimes called substitution, and examples of it have had very important influence in the history of the development of organic chemistry. A very important example is furnished by water and chlorine. Some of the chlorine reacts by substitution with the water according to the equation:



The reaction does not go very far in the direction indicated by the arrow and but small quantities of hydrochloric acid ( $\text{HCl}$ ) and hypochlorous acid ( $\text{HClO}$ ) are formed because the reaction is reversible like that of hydrogen and iron oxide. (See p. 67.) This opens up a very important question — that of equilibrium — which is discussed in the next chapter. If the water and chlorine are placed in the sunlight the hypochlorous acid decomposes, giving oxygen:



The instability of hypochlorous acid will be more fully discussed later, but must be mentioned here because it is the reason for one of the most important uses of chlorine, that of bleaching (*q.v.*) (p. 193).

It will be noted from the previous discussion that chlorine is an extremely active element chemically. Indeed, at least at ordinary temperature, it is more active than oxygen. Yet a point not mentioned previously ought not to be omitted. Carefully dried substances react very slowly, or perhaps not at all, with carefully dried chlorine. This is of interest because chlorine, if moist, attacks iron vigorously, but *dry* liquid chlorine may be kept indefinitely in the iron cylinders of commerce.

**Uses of Chlorine.** — Chlorine finds extensive technical application as a bleaching agent, as a disinfectant, as a deodorant, and in metallurgical operations. As a bleaching agent its value lies in the formation of hypochlorous acid when dissolved in water and



its action in this connection will be discussed in connection with that acid (*q.v.*). It owes its value, both as a disinfectant and deodorant, to its activity as a substituting agent, when used with hydrogen compounds. The protoplasm, of which bacteria almost wholly consist, is so rendered solid and incapable of motion. Odoriferous substances are usually easily oxidizable substances, and consequently deodorization may be produced not only by substitution, forming odorless substances, but by oxidation. The use of chlorine in metallurgy is ordinarily due to the formation of soluble chlorides by union of the metal with chlorine. The most important chlorination process is concerned with gold extraction (*q.v.*). Chlorine is also used in various manufacturing operations, such as the preparation of bromine (*q.v.*). Chlorine has recently found a new use; in warfare as a suffocating gas. (See History of the World War.)

**Compounds of Chlorine.**—The compounds of chlorine are extremely important from various standpoints and many are of large technical application. The discussion of various classes will be taken up in other connections, and the present discussion confined to chlorides. Of the chlorides the one from which all the others may be considered as derived is hydrogen chloride. Its importance is such that the discussion will be in considerable detail.

#### HYDROCHLORIC ACID

The substance is not found free in nature except under very unusual circumstances. It is reported as occurring in the water from various volcanic regions and also occurs in the gastric juices of animals to about 0.1 per cent. Its compounds with metals, chlorides, are very abundant and from these it is obtained. (See preparation.)

**History.**—Hydrochloric acid in solution in water seems to have been known to the Arabian alchemists, as shown by the writings of Geber, but under the name "spirit of salt" is first described by Basil Valentine (1644), who appears to have made it by distilling salt and green vitriol. In 1648 its preparation by the action of sulfuric acid on salt was described by the alchemist, Glauber; hence the name Glauber's salt for the other product, sodium sulfate. Priestley, the discoverer of oxygen, first collected the gas, which he called "marine-acid air," over mercury. The solution in water

was called muriatic acid, a name by which it is still known commercially, because of its preparation from sea salt (*sal murias*). It was of little value, *i.e.*, its uses were but slightly developed, until the discovery of the LeBlanc Soda Process (*q.v.*) made its preparation extremely cheap, since it was a by-product. Indeed, the gas was allowed to escape as a waste product until collection in water was required by law as an abatement of a nuisance. The necessity of disposing of this by-product stimulated the study of its uses and at present the original process (LeBlanc Soda Process) lives largely by reason of the value of the material formerly thrown away.

**Preparation.**— There are many means of preparing the acid and they may be conveniently grouped into three general methods.

1. If hydrogen and chlorine are brought together in the dark no change takes place, but if in diffused light the union goes on slowly until without change of volume the conversion into hydrogen chloride is complete,  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ . If in direct sunlight or the light of burning magnesium, the action takes place with extreme rapidity and because of the high temperature produced (the heat of reaction is 22,000 cal.), there is a sudden and large expansion of volume, an explosion. If a jet of burning hydrogen be immersed in chlorine, it will continue to burn, with a change of color of the flame, and dense clouds of gaseous hydrochloric acid are formed. The formation of a fog is explained on p. 125.

2. A cheaper method of making the gas is to treat a metallic chloride with an acid. The chloride most frequently employed is common salt ( $\text{NaCl}$ ) and the acid used is, ordinarily, sulfuric acid. Thus:

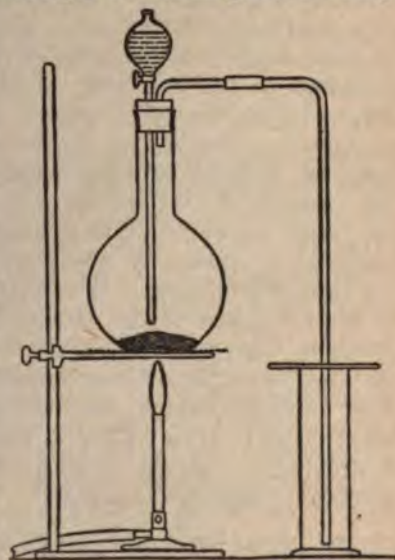
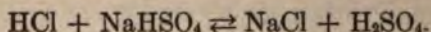


FIG. 35.

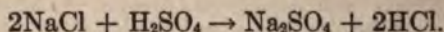


This experiment is ordinarily carried out using dry salt and concentrated sulfuric acid (Fig. 35). Dilute sulfuric acid may not be used if a large yield of hydrogen chloride is required, since the gas is very soluble in water and the products have a tendency to react as indicated:



This reversibility of reaction is frequently encountered and the principles involved will be shortly discussed. (See Chap. VII.)

If a limited amount of sulfuric acid be employed, or if the components are warmed, the products are hydrogen chloride and sodium sulfate, as indicated:

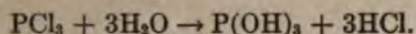


Any metallic chloride will react as does sodium chloride, but it is not a matter of indifference which is employed, even though no attention is paid to their relative cost. The rate of evolution varies with the chloride used and the cause of the variation is, in part at least, variation in the solubility of the chlorides. It is obvious that before action can occur contact must be secured and intimacy of contact is a function of the solubility. That this is not the only cause of variation will later appear. (See Chap. IX.) It is also not a matter of indifference, aside from cost, what acid is employed, for, while we may obtain hydrogen chloride by treating salt with phosphoric, sulfuric or acetic acids, there is a great difference in the rates of evolution. This variation is due in part to a variation in what is known as the "strength" of the acids, explained more in detail in Chap. IX. It must also be observed that certain acids may not be employed because the acid used and the hydrogen chloride mutually destroy each other. This is the case with nitric acid. (See p. 127.) Finally, the acid must be less volatile than hydrochloric acid, else no satisfactory completion of the reaction is attained. (See next chapter.)

The student will observe that we are sadly in need of the facts presented in the following chapter in order to make this series of statements fully satisfactory.

3. The acid may further be prepared by treatment of certain chlorides, non-metallic chlorides, or compounds of similar type, with water. (See also p. 81.) This method is obviously not of practical use, since the chlorides are more expensive than the acid,

but frequently the process is carried out in the course of operations required for other ends. The acid is then regarded as a by-product. The most convenient illustration is the decomposition of phosphorus trichloride with water.



**Physical Properties.—**

Specific gravity, 1.269.

Density ( $\text{H}_2 = 1$ ), 18.23.

Weight of 1 l., 1.641.

Solubility in water  $0^\circ \text{C.}$ , 52,500 vol. to 100.

Maximum boiling point of aqueous solution,  $110^\circ$  (20.24 per cent HCl).

Specific gravity of aqueous solution, 1.2 (40.00 per cent HCl).

Crit. temp.,  $52^\circ$ .

Boiling pt.,  $-83.7^\circ$ .

Freezing pt.,  $-112.5^\circ$ .

Sp. gr. of liquid, 0.908.

Heat of solution, 17,400 cal.

The pure hydrogen chloride is a colorless gas which "fumes" strongly in contact with moist air. This appearance of fog is due to the fact that with the moisture of the air the gas forms a solution which has a smaller vapor tension than either water or the acid, and usually less than the vapor pressure in the air in which the solution is formed, hence minute drops of liquid form and these droplets are visible.

The weight of 1 l. of the gas, if multiplied by the molecular volume, 22.4, gives a molecular weight of 36.76, while the sum of the atomic weights of its constituents ( $35.458 + 1.008$ ) gives the value, 36.466. The close approximation of the two values corresponds to what is to be expected from the kinetic molecular hypothesis which leads to the expectation that gases approximate more closely to exact conformity to Boyle's and Charles' laws when they are far from their boiling point, which is in the case of hydrogen chloride —  $83.7^\circ \text{C.}$

The gas dissolves in water to a very remarkable extent. 1 cc. of water at  $0^\circ$  will absorb about 525 cc. of the gas (approximately 46 per cent HCl). At  $15^\circ \text{C.}$  the volume relation is approximately 475 of gas to 1 of water (42.9 per cent). The specific gravity of



the solution varies with the concentration and in the appendix to the laboratory manual is given a table of specific gravities corresponding to various concentrations.

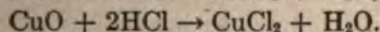
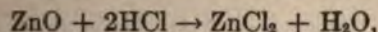
A concentrated solution of the gas in water, if exposed to the air, loses gas until a concentration of approximately 20 per cent is reached. The gas so given off, of course, fumes in moist air for the reason previously given. If the solution be heated a loss of gas also occurs until at 110° C. a mixture of 20.24 per cent HCl and 79.76 per cent H<sub>2</sub>O is reached. If, on the other hand, a more dilute solution be heated, water is given off until the same concentration and boiling point is reached. This relation corresponds almost exactly to the formula  $\text{HCl} \cdot 8\text{H}_2\text{O}$ , (1 : 7.98), and the question immediately arises as to the reason for discussing this relation as a physical property when it appears that so definite and stable a hydrate is formed, especially when we consider also the heat of solution in the light of an energy change accompanying chemical change. The answer lies in the fact that not only does the relation vary as the atmospheric pressure varies, becoming 23 per cent HCl at 0.066 atmosphere, and 18 per cent at 2.6 atmospheres, but also that the freezing point of solutions shows no compound corresponding to this composition. (See the phase rule, and also Rupert, Jour. Am. Chem. Soc., 1911.) The matter has been carefully investigated and the situation illustrates the futility of attempting a sharp division between chemical and physical changes.

**Chemical Properties.** — Hydrogen chloride as a gas is an extremely stable substance, which only begins to dissociate into its elements at 1500° C. It irritates the mucous membrane when inhaled and is, under ordinary circumstances, neither combustible nor a supporter of combustion. Neither as a *dry* gas nor as a liquid does it show the activities characteristic of its solution in water. *Dry*, it neither reacts with metals nor in other ways shows the properties associated with the term "acid." For this reason there is a strong tendency on the part of chemists to use, for the gas the term hydrogen chloride, a perfectly correct term, and to confine the name hydrochloric acid to its solutions in water. This distinction is academic, however, since, as we shall see, the same distinction holds for all acids, *i.e.*, no substance shows acid properties except in the presence of water. (See p. 177 *et seq.*)

Moist hydrochloric acid gas reacts with many substances, *e.g.*,

of the very fruitful hypotheses, the ionization hypothesis, was manufactured in part for the purpose of furnishing an explanation of the catalytic effect of water. (See p. 185.) For the present then we may content ourselves by discussing the chief activities of the substance under two heads.

**Reaction as an Acid.** — Hydrogen chloride in solution in water has a taste, affects the color of many substances, such as litmus, methalein, cochineal, etc., and reacts with metals preceding it in the electromotive series with varying rapidity, liberating hydrogen and forming chlorides of the metals. It also reacts with many oxides, indeed, nearly all those known as metallic oxides, forming water and a chloride of the metal, *e.g.*,



With hydroxides of metals it also reacts to form chlorides and water, *e.g.*,  $\text{Fe(OH)}_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$ . It will be observed that in these reactions we may express the quantitative relations involved without mentioning its presence. The student should also recall that various methods of making chlorides are available in addition to the methods just discussed.

**Reaction as a Reducing Agent.** — In discussing the preparation of chlorine we found one of the more frequently employed methods is the oxidation of hydrogen chloride, either dry or in solution. Since oxidation and reduction are antithetic terms, we



Aqua regia, which is made by mixing hydrochloric acid and nitric acid in the molecular proportions indicated by the equation, therefore, owes its activities to the presence of chlorine. (See p. 119.)

**Uses of Hydrochloric Acid.**—The uses of hydrochloric acid are very varied. The most important is the manufacture of chlorine, which, in turn, is extensively used. It is also used directly or indirectly for manufacture of chlorides of the metals which do not occur in satisfactory form or quantity in nature. It is used to produce hydrogen for commercial purposes, in soldering processes and countless other minor operations.

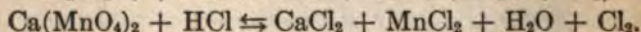
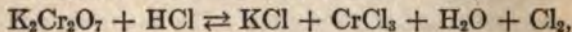
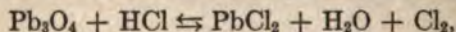
**Exercises.**—1. When sea water evaporates what facts determine the order of deposition of the salts?

2. How much would it cost for materials to make a pound of chlorine if the cost of salt is 2 cents per pound, sulfuric acid, pure, 6 cents per pound, and manganese dioxide, 60% pure, 10 cents per pound? Assume that the impurities of the reagents are without effect upon each other.

3. If in the electrolysis of chlorides in solution the products of reaction are allowed to interact, what is formed? (See p. 192.)

Explain why the volume of chlorine liberated by the electrolysis of hydrochloric acid is at first less than that of hydrogen.

4. On the assumption that the following equations represent the materials involved in reactions represent correctly the amount



5. What are the objections to collection of chlorine over water, (b) mercury, (c) by displacement of air?

6. Make a statement of the facts involved in the liquefaction of chlorine and the assumptions made in explanation of the process.

7. Write equations showing the combining relation of chlorine with phosphorus, sulfur, sodium, zinc, and carbon. Which of the compounds formed are exothermic?

8. By the use of reference books write a brief discussion of the practical use of chlorine in (a) metallurgy or (b) as a disinfectant.

9. Make equations representing the action of sulfuric acid on  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ , and  $\text{AlCl}_3$ .

10. Calculate the exact formula of the hydrate of hydrochloric acid which boils at  $110^\circ$ , composition 20.24%  $\text{HCl}$ .

11. Make a complete list of the methods available for making acids so far as they have been met in the laboratory or text-

2. Catalogue in tabular form the physical and chemical properties of chlorine and of hydrochloric acid.



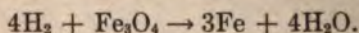
## CHAPTER VII

### REVERSIBLE REACTIONS AND EQUILIBRIUM

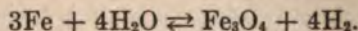
SEVERAL reactions have already been met in which, under given conditions, a certain set of materials react to produce others while at the same time the products of these reactions are capable of so reacting as to produce the original substances. An example is furnished by the behavior of steam and iron. This reaction may be expressed:



This reaction takes place when steam is passed over hot iron. If, however, the conditions are so altered that hydrogen is passed over heated iron oxide the course of the reaction becomes



Such reactions are called *reversible* and far from being exceptional are quite the rule. If we remember that equations do not show the conditions of reaction we may express both reactions by a single equation, using double arrows to express reversibility. Thus:

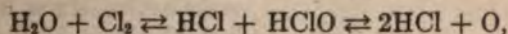


Since ordinarily in performing a chemical operation, the object is to obtain as much of a given substance as possible, and since the vast majority of operations are of the reversible type, it is obviously important to know what principles govern this reversibility, and to know when the opposing tendencies balance each other, that is, when under fixed conditions equilibrium of reaction is reached. It is the purpose of this chapter to make these points as clear as may be with the assumed degree of chemical information of the reader.

If we study closely the reaction just mentioned, we shall observe first that no appreciable reaction takes place, in short intervals of time at least, if steam is passed over cold iron. If, however, the iron be heated, a portion of the steam will be decomposed. Since

we are already aware that the effect of increased temperature is to increase the speed of reactions, we may assume that there exists an inherent tendency toward decomposition in the direction indicated by the arrow  $\rightarrow$ , which tendency is accelerated by rise of temperature. It is, however, obvious that this explanation is not sufficient, for were the sole cause of the reaction the greater affinity between iron and oxygen as compared with hydrogen and oxygen, we should be left in a hopeless quandary in attempting similarly to explain the reverse reaction, since we should be forced to assume in that case greater affinity between hydrogen and oxygen than between iron and oxygen. We may observe, when the reaction goes toward the right, as indicated in the equation by the arrow  $\rightarrow$ , that steam is present in unlimited quantities, and any steam which is decomposed is constantly replaced from the boiler, while any hydrogen produced is immediately removed from any possible contact with the iron oxide already formed. It may well be then that the direction of the reaction is influenced by relative concentrations of steam and hydrogen, and when that of the latter is zero the reaction proceeds smoothly in the direction  $\rightarrow$ . This line of thought is supported by the consideration of conditions necessary for the reaction in the reverse direction, indicated by the arrow pointing to the left ( $\leftarrow$ ). Here we have an unlimited supply of hydrogen constantly replaced, while the steam formed is removed as rapidly as it is produced. Granted then a tendency to react between iron and oxygen and between hydrogen and oxygen, the rate of which reactions may be influenced by changes in temperature, it seems clear that *the direction in which reaction takes place is determined by the relative concentrations of the reacting materials*. This conclusion is confirmed by the study of all the reversible reactions we have encountered.

A few examples may be cited, and in subsequent study the reader is urged to look for similar cases, since the principle is of vast importance and of perfectly general application. In the case of the reaction between chlorine and water,

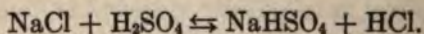


when we adjust conditions so that the hypochlorous acid is decomposed as fast as formed, *i.e.*, by placing the apparatus in bright light, the concentration of the latter is kept constantly at practically zero, while the concentration of the chlorine, however small, is relatively greater. The result, therefore, of exposing a



solution of chlorine to the sunlight is the decomposition of water. In this case, the influence affecting the speed of the reaction is the effect of sunlight upon the stability of hypochlorous acid. When we bring oxygen and hydrochloric acid together under the conditions of Deacon's process, the reverse action takes place; and in this case the speed of reaction is brought up to a desirable rate by the rise of temperature, coupled with the catalytic effect of the presence of copper salts. In Deacon's process the concentration of the chlorine and steam are, at the point where rapid reaction takes place, kept at a minimum, since they are continuously removed by the incoming flow of air and hydrogen chloride.

Another example is furnished by the reaction between salt and sulfuric acid, which may be written reversibly:



If the conditions are such that as fast as any hydrogen chloride is produced, it is removed from any probable contact with the sodium hydrogen sulfate, which is also formed, there can be no opportunity for reaction in the reverse direction. These conditions are obtained when we treat the dry salt with concentrated acid. (Fig. 36.) In this case, the reaction proceeds at a reason-

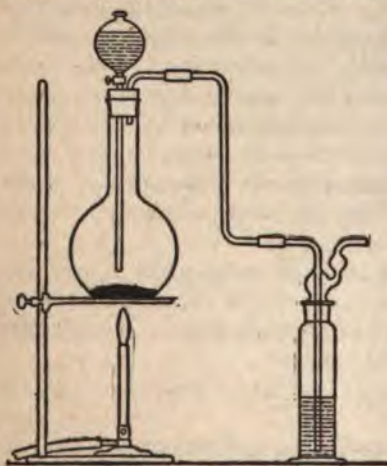


FIG. 36.

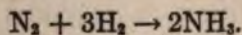
able rate at the ordinary temperature. If, on the other hand, we take sodium hydrogen sulfate of large concentration, *i.e.*, a saturated solution, and introduce hydrogen chloride under pressure, we favor the tendency to react as indicated by the reverse arrow,  $\leftarrow$ . The necessary result is the formation of some salt and sulfuric acid. If sufficient salt is formed to exceed its solubility, the precipitation favors the reverse action, since, by the kinetic hypothesis, it is to be expected that opportunity of reaction between a solid substance and a liquid is less than when both are

in a liquid state. Other examples of reversibility already encountered might be cited, but sufficient has been said to make clear

the principles involved, and the student is, perhaps, eager to learn what occurs when the products of a reaction are not removed and reverse tendencies are present. We must hasten to gratify this desire, but not before remarking that it should be clear that to produce as complete reaction in a given direction as possible the operator must study the conditions tending to produce the removal from the field of operations of one or more of the products, as rapidly and as completely as may be.

**Equilibrium.**— When the products of a reversible reaction are not removed from contact with each other a few moments consideration makes it evident that the rapidity of the reverse action increases, while the direct reaction diminishes in rate, since as we have seen, the rate, other things being equal, depends upon concentration. This, of course, assumes that no new addition of original materials keeps up the supply, and no removal of material formed diminishes the rate of reversal. It follows, then, that at some point the rates of reaction are equal and the considerations brought out by the kinetic hypothesis lead to the conclusion that no change will be observed as taking place. This condition is known as equilibrium of reaction.

We find it convenient to distinguish two sorts of equilibrium. One, in which all the factors form a homogeneous mixture and are, therefore, in the same physical state, *i.e.*, all gaseous, all liquid or all solid, is spoken of as an *homogeneous equilibrium*. The other, in which one, or more, of the components exists in more than one state is an *heterogeneous equilibrium*. All the components of either sort of equilibrium taken together are known as a *system*. An example of an equilibrium system will perhaps make all this clear. If we place dry hydrogen and dry nitrogen in a eudiometer, making the relative volumes 3 : 1, they may unite to form ammonia.



The rate of combination at room temperature is however infinitely slow. If we pass electric sparks through the gases the reaction takes place at measurable speed though still somewhat slowly. (See Fig. 37.) The sparking may, however, be continued until no further change of volume takes place. If the reaction were complete we ought to obtain from four volumes of the mixed gases two volumes of ammonia, but such is not the case. In a given



experiment we may find a change from 24.1 cc. to 23.86 cc. If, on the other hand, we spark dry ammonia under the same conditions we obtain an increase in volume, and indeed an expansion from 12.05 cc. to 23.86 cc. We have then a reversible system consisting of the gases, nitrogen, hydrogen, and ammonia, a homogeneous system in equilibrium, when continued sparking produces no change

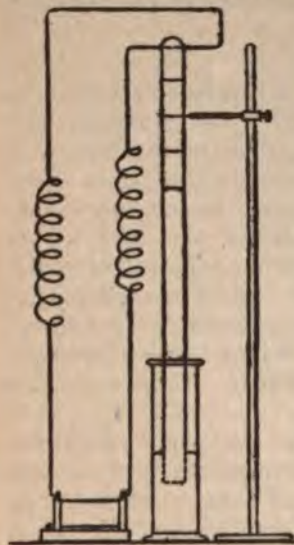
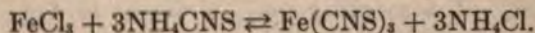


FIG. 37.

in volume. It is apparent, in terms of the kinetic hypothesis, that the rate of change from nitrogen and hydrogen to ammonia produced by sparking diminishes, and that the rate of decomposition of ammonia molecules under the same conditions increases as the number available diminish or increase. No change in the relative numbers will be apparent when these rates are equal, though the individual molecules may be changing partners at ever so great a speed. When equilibrium in this system is established it may be disturbed and the reaction caused to proceed in one or other direction by change of concentration of one of the factors, *e.g.*, we may introduce a little sulfuric acid into the eudiometer; ammonia unites at once with the acid, and so is removed from the system. The formation of ammonia by sparking is no

longer counterbalanced by decomposition, hence continued sparking results in the complete conversion of all the nitrogen and hydrogen into ammonia.

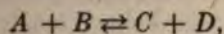
Another example of homogeneous equilibrium will be particularly appreciated because the color effects render the situation visually apparent. Ferric chloride ( $\text{FeCl}_3$ ) and ammonium sulfocyanate ( $\text{NH}_4\text{CNS}$ ) react when in solution to form ferric sulfocyanate and ammonium chloride, and the former is blood red in color. If we mix dilute solutions of the first two substances in equivalent amounts, we may express the change reversibly:



Since the materials are all soluble, we have a homogeneous system. That the principles we have outlined hold may be shown by

dividing the solution into several parts. If to one we add some concentrated solution of ferric chloride, thus increasing the concentration, the color deepens, showing that increased formation of  $\text{Fe}(\text{CNS})_3$  has taken place; addition of concentrated ammonium sulfocyanate to a second portion also deepens the color, while addition of concentrated ammonium chloride diminishes the color. The student should appreciate the fact that the deeper color denotes the presence of excess molecules of ferric chloride and of ammonium sulfocyanate only because the addition of each causes the same change.

**Law of Homogeneous Equilibrium.**—We may obtain a mathematical expression of the relation between concentration and the point of equilibrium in homogeneous systems very simply as follows: Consider the general reaction of the type



where the components form a reversible reaction and are present in homogeneous mixture. At any given constant temperature, the speed of reaction of  $A$  upon  $B$  depends upon their nature (*i.e.*, upon the driving force of all reactions, ordinarily called affinity, and which is constant when the temperature is constant), and upon the concentration. Concentration is ordinarily expressed in terms of moles per liter. If, then, we have one mole of  $A$  and one of  $B$  per liter, the rate of reaction ( $V$ ) at a given instant may be expressed  $V = F$ , where  $F$  is the affinity constant. That is, the concentration is unity. If, however, the concentration of  $A$  is  $C_1$  and of  $B$  is  $C_2$ , then

$$V = C_1 \times C_2 \times F.$$

Similarly, if we consider  $C$  and  $D$ , the velocity of their reaction in the opposite direction ( $V'$ ) is expressed  $V' = C_3 \times C_4 \times F'$ , where  $C_3$  and  $C_4$  represent the concentrations of  $C$  and  $D$  respectively and  $F'$  the affinity constant of  $C$  and  $D$ . When equilibrium ensues  $V = V'$ , and consequently  $C_1 \times C_2 \times F = C_3 \times C_4 \times F'$ , or

$$\frac{C_1 \times C_2}{C_3 \times C_4} = \frac{F'}{F}.$$

The nature of the substances as affecting each other, their mutual



affinities, remaining the same at a fixed temperature, we may substitute for the ratio  $\frac{F'}{F}$  the constant  $K$  and have the expression

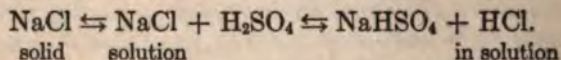
$$\frac{C_1 \times C_2}{C_3 \times C_4} = K.$$

This is the fundamental law of chemical equilibrium. It is evident that if we have a reaction  $3A + B \rightleftharpoons C + D$ , we may write it  $A + A + A + B \rightleftharpoons C + D$ , and, following the same manner of derivation as above, obtain:

$$\frac{C_1^3 \times C_2}{C_3 \times C_4} = K.$$

This relation expressed in words is: *The point of equilibrium of a balanced action in a homogeneous system depends upon the ratio of the products of the concentrations of the substances reacting in one direction to the product of the concentrations in the other direction, and upon the affinities of the substances, the latter being a constant at a fixed temperature.*

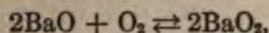
**Heterogeneous Equilibrium.**—When we have a system which is not homogeneous some modification of the above law is involved. For example, if we consider the saturated solution of sodium chloride with an excess of solid chloride in equilibrium with the other components of the system the reaction may be expressed as follows:



First let us suppose the system not in equilibrium and consider only the relation between the solid and dissolved chloride. If  $C'$  expresses the concentration of sodium chloride as a solid, and  $C''$  that of the solution, the rate of solution may be expressed by  $V = C'K$ , and the rate of precipitation  $V' = C''K'$ , where  $K$  and  $K'$  represent the tendencies of salt to go into and out of solution respectively. When there is no reaction apparent, i.e., equilibrium, then  $V = V'$ , or  $C'K = C''K'$ , or  $\frac{C'}{C''} = \frac{K'}{K}$ , and consequently  $\frac{C'}{C''} = K''$ . Expressed in words: *The point of equilibrium in a heterogeneous system depends upon the nature of the substances, a fixed value at a given temperature, and the ratio of their concentrations.*

We have already had several illustrations of this law. For example, the concentration of a solid is its specific gravity, which

for most compounds is a fixed value. The solubility of a solid in a solvent is then a fixed value at a given temperature. Again, the concentration of gases is a function of their pressure. The solubility of gases is then also a function of the pressure. (See Henry's law.) Again, in Brin's process, when equilibrium at  $700^{\circ}$  is reached in the reaction,



if the concentration of oxygen is diminished by pumping, the reaction must reverse and oxygen be liberated. The student will derive both pleasure and profit in seeking other illustrative cases.

**Speed of Reactions.**—The rate of any chemical reaction which takes place in a homogeneous system, at a constant temperature, is, as we have seen, proportional to the concentration of the reacting substances at a given moment. It follows, therefore, that as the concentration of the components of a reaction progressively alters, the speed of reaction also alters. The character of this relation varies with the entrance of one, two or more molecules into the reaction. For what is known as a monomolecular reaction, of the type  $A \rightarrow B + C$ , the relation is expressed by the equation,

$$S = \frac{1}{t} \log_e \frac{C_1}{C_1 - x}.$$

In this equation  $C_1$  represents the original concentration of  $A$  at the beginning of the reaction,  $x$  the change in concentration in the time  $t$ , and  $S$  the velocity constant, *i.e.*, the velocity of the reaction when the concentration is unity. The student will find but little use for this relation in an elementary course and is referred to texts on physical chemistry for the derivation of the equation (see Bigelow's *Theoretical Chemistry*, p. 353).

It is essential, however, for the student to observe the fact that in ordinary reactions the original concentration is not maintained. With diminishing concentration the rate of reaction decreases. Consequently for *absolute* completion of a reaction an infinite time is required. For a monomolecular reaction the time required for so-called complete reaction (0.999 parts of the original amount) is ten times that required for the first half of the reaction to take place (see Bigelow's *Theoretical Chemistry*, p. 356). The time required for "completion" of a monomolecular reaction may, therefore, be calculated by determining the time required for fifty per cent com-



pletion. This is the meaning of the "half-period" so often referred to in discussions of radio-activity (*q.v.*)

**Illustrative Cases.** — We are now in position to appreciate more fully the meaning of some of the reactions already studied. For example, phosphorus burns more rapidly in oxygen than in air, because the concentration is five times greater and the rate is still further increased because, since it burns more rapidly, the ratio of production to loss of heat is greater and a higher temperature is reached. Iron burns in oxygen and not in air, in a laboratory experiment, because the kindling temperature may be maintained by the increase of rate secured by increased concentration, while in air under ordinary conditions the rate is too slow. By excessively high initial temperature, as in a conflagration, the requisite rate may be maintained; hence steel structures may burn in air. The diminution of concentration immediately surrounding a bit of steel rod may be overcome by using the same weight of steel in the form of wool, which burns fiercely. The student is again urged to seek other cases illustrative of change in speed of reaction with change of concentration of the reacting substances.

***The Effect of Changes of Temperature Upon Equilibrium.***—

In the considerations involved in the preceding discussion of equilibrium, it was carefully pointed out that the temperature of a system must be constant in order that the conclusions reached be correct. The reason for this is that not only is the speed of reactions affected, as is to be expected by the kinetic molecular hypothesis, by change of temperature, but the affinities of the reacting substances as well. For example, mercuric oxide at high temperatures is less stable than at ordinary temperature. It is then to be expected that with change of temperature the ratio  $\frac{K'}{K}$  (see p. 136) will change and,

therefore,  $V$  and  $V'$  be affected differently. There has been found a generalization which applies to this effect of temperature, which is known as van't Hoff's law of mobile equilibrium. It is, in general terms, *the effect of increase of temperature is to promote an endothermal reaction and resist an exothermal one.* The effect of an increase of temperature on a system in equilibrium is, therefore, to increase the relative quantities of substances which are produced by absorption of heat and hence move the point of equi-

librium in this direction. A good example of the situation is found in the case of cyanogen, an unstable endothermic compound, produced in the distillation of coal, and in blast furnaces. Indeed, the generalization of van't Hoff (1884), apparently developed from a study of the solubility of salts in water, is but a special case of a generalization of much wider application, which includes the effects of change of concentration, pressure, temperature, etc. It was stated in 1888 by Le Chatelier and is sometimes known as the Theorem of Le Chatelier. It may be formulated: *Any system in equilibrium, physical or chemical, when subjected to a stress moves or tends to move in such manner as to undo the stress.* We shall attempt to keep this principle well in the foreground as we proceed.

**The Effect of Catalytic Agents Upon Equilibrium.**—The presence of catalytic agents in a reaction affects the rate at which a given reaction takes place, but, according to Ostwald, cannot produce a reaction where one is not already proceeding. They, therefore, do not affect the relative proportions of the components of a reaction, when in equilibrium, though clearly the time required by a given system to reach equilibrium is vitally affected.

**Exercises.**—1. Make a list of ten reversible reactions selected from preceding chapters. Write the equations and discuss the conditions under which the reaction goes to the right ( $\rightarrow$ ) and to the left ( $\leftarrow$ ).

2. Write the equation for the reaction between zinc and sulfuric acid and explain why the reaction goes to completion with exhaustion of the supply of either the zinc or sulfuric acid.

3. If we have a reversible reaction in equilibrium, discuss all the ways in which the equilibrium may be disturbed.

4. In the calcination of metals explain from the equilibrium standpoint why an open crucible is to be preferred to a closed crucible.

5. Distinguish between homogeneous and heterogeneous systems. Illustrate by equations, equilibrium reactions in each.

6. Formulate in terms of the law of molecular concentrations the dissociation of steam at high temperatures. How would an increase in pressure displace the equilibrium? Why?

7. What factors influence the velocity of a chemical change? Of these factors which are subject to the control of the experimenter?

8. Distinguish between the terms "reversible" and "equilib-



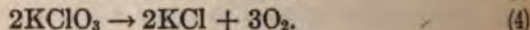
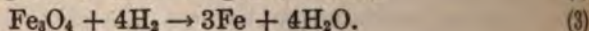
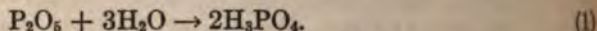
rium" as applied to reactions. What is meant by the expression "the reaction goes to completion"? Are complete interactions always non-reversible? Illustrate by an example.

9. How does an increase in temperature influence the following equilibrium reactions?

- (a)  $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$   
 (b)  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$   
 (c)  $2\text{BaO} + \text{O}_2 \rightleftharpoons 2\text{BaO}_2$

10. In the reaction between salt and sulfuric acid how is the equilibrium condition influenced (a) by increasing concentrations of sulfuric acid, (b) by increasing concentrations of hydrochloric acid, (c) by increasing temperature?

11. Explain the completeness of the change in the following interactions:



Which of these reactions are reversible and under what conditions may the reversal be effected?

12. In the reaction  $A + B \rightleftharpoons C + D$ , if the action of  $A$  upon  $B$  is exothermic, what is the effect of change of temperature upon the point of equilibrium?

13. If in the reaction  $A + B \rightleftharpoons C + D$  all the substances are gaseous and conform to the gas laws, what effect on the point of equilibrium by change of pressure can be predicted, temperature being kept constant?

14. If we have the reaction  $A + B \rightleftharpoons C + 2D$ , what effect upon the point of equilibrium is produced by change of pressure, the same assumptions being made as in problem 13?

## CHAPTER VIII

### THE HALOGEN FAMILY

COMMON salt, in mineral form, is known as halite. The sodium compounds of several elements resemble halite in that they are of like crystalline form, color, etc., and are similar in taste. These elements are, therefore, known as **halogens**, or salt formers. The elements are fluorine, chlorine, bromine and iodine. They possess so many properties in common that the resemblance entitles them to be called the "halogen family." It is the purpose of the present discussion to present them to the reader, not separately, but in their relation to each other, so that the recently acquired knowledge concerning chlorine may both aid in their study and be itself also intensified.

**Occurrence.** — None of the elements in the family occur free. **Fluorine** (F) occurs rather widely distributed, but chiefly in the form of calcium fluoride ( $\text{CaF}_2$ ), known variously as fluspar, fluorite and blue john. It is also found in considerable masses as cryolite ( $\text{Na}_3\text{AlF}_6$ ) and as apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ). The most interesting occurrence of fluorine is in the human body, where traces amounting to four or five parts per hundred thousand are found in the bones, hair, teeth, nails, etc.

**Bromine** (Br) is found mainly in sea water and the salts deposited by its evaporation. The quantity found in various salt deposits and also the quantity in mineral water derived from such deposits varies greatly. Only the richer sources are utilized for its manufacture. The chief commercial source is the brines derived from the purification of the salts from the Stassfurt mines, though considerable quantities are obtained as a by-product from the manufacture of salt in America.

**Iodine** (I) occurs as sodium iodide ( $\text{NaI}$ ) to the extent of from 0.1 to 0.3 per cent in the ash of sea weeds which was until rather recently the chief source of supply. It also is found in minute quantities in sea water and in various plants and animals, chiefly aquatic. Its presence in mineral springs is fairly frequent and



its presence in the thyroid gland of mammals is of considerable physiological significance. At the present time most of the iodine of commerce is obtained in the purification of crude Chile saltpeter ( $\text{NaNO}_3$ ), known as **caliche**, in which it occurs as sodium iodate (see iodic acid),  $\text{NaIO}_3$ .

**History.** — The story of the discovery and isolation of these elements is one of the most interesting in chemistry. Shortly after the publication of the demonstration of the elementary nature of chlorine in 1810 by Davy, a French soap and saltpeter manufacturer, Courtois, heated the mother liquor from an aqueous extract of kelp, the ash of seaweed, with sulfuric acid. The violet vapors that formed condensed in the receiver in brilliant black scales. He communicated this discovery to Clement and Desormes, who in 1813 published the results of a study of the substance. In 1814, Gay-Lussac published an investigation in which he demonstrated its character as an element and its relationship as a non-oxygen acid forming factor. He gave the new element its name, iodine (from *ἰώδης* = violet). His conclusions were confirmed by Sir Humphry Davy.

The element bromine was first isolated by Justus von Liebig, but by him considered a mixture of iodine and chlorine. In 1826, Balard extracted with ether a yellow liquid obtained by treating the mother liquor from salt manufacture with chlorine. The ether solution eventually yielded a reddish brown liquid, which proved to be an element closely allied in properties to iodine and chlorine and called, by reason of its powerful and offensive odor, bromine (from *βρῶμος* = a stench).

The fact that sulfuric acid and a mineral known as fluorspar, when warmed together, produce fumes which attack glass was known at least as early as 1670, and in 1771 Scheele recognized fluorspar as the calcium salt of an acid, since called hydrofluoric acid. The acid was isolated by Gay-Lussac in 1807. In 1810, Ampere, he of electrical note, suggested to Davy that hydrochloric acid and hydrofluoric acid were analogous and that the element characteristic of the latter should be named fluorine. Davy himself and many after him labored in vain to effect its isolation, but no success was attained until 1886, when Moissan, a distinguished French chemist (popularly known by reason of his manufacture of diamonds), hit upon the scheme of electrolyzing potassium fluoride in solution in liquid hydrofluoric acid. (See Fig. 38.) The result

the isolation of a light yellow gas with all the properties it expected to possess. It is interesting to note that between when Ampere wrote his letter to Davy, and 1886 chemistry was so far developed that chemists were able to know in advance of its isolation not only of the existence of the element, but practically as much about its properties as became known after it had been isolated. The chief single advance was the discovery which conferred this gift of prophecy was the periodic law (*q.v.*).

**Preparation.** — Attention was called to chlorine to three general methods of preparation: (1) heating of chlorides, (2) electrolysis of chlorides, (3) oxidation of hydrogen chloride. Since the three methods under discussion are similar to those of fluorine, it is of interest to note how these methods are applicable. As regards the first method,

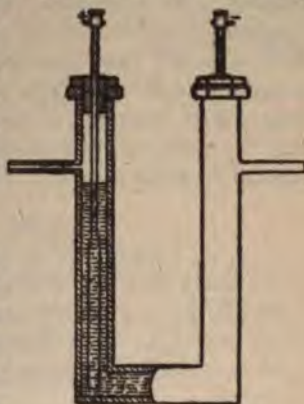
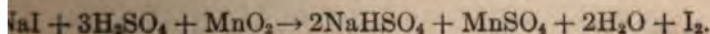
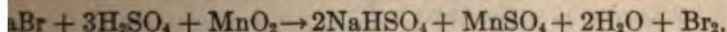


FIG. 38.

more need be said than that it fails with fluorine by reason of the great activity of the latter and is not used for iodine and bromine for reasons of economy solely.

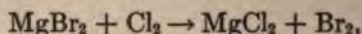
As has been mentioned, electrolysis serves for the preparation of fluorine, provided pains be taken to use materials and apparatus unaffected by fluorine at the temperature employed. If an aqueous solution of a fluoride be electrolyzed, the product at the anode is not fluorine, but oxygen, and if fused fluorides are employed the result is but the production of fluorides of the materials in the apparatus employed. Electrolysis of iodides and bromides is in the liberation of the elements and would be employed in their manufacture were not other more economical or more convenient methods available.

Oxidation of hydrofluoric acid fails as a method of preparation of fluorine chiefly by reason of the great chemical activity of the element. The method can be and is employed for both iodine and bromine and the equations illustrating its application are analogous to those for chlorine and the conditions are similar, thus:



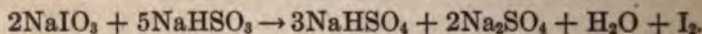


A fourth method by which chlorine can be prepared may now be introduced. If a chloride such as sodium chloride be treated with fluorine the reaction,  $2\text{NaCl} + \text{F}_2 \rightarrow 2\text{NaF} + \text{Cl}_2$ , takes place very rapidly. In a precisely similar manner, if bromides or iodides be treated with chlorine, the less active elements are liberated and the method is the one employed for the most part, at present, for their commercial preparation, *e.g.*, a stream of a solution containing magnesium bromide is allowed to trickle down a tower filled with earthenware balls, or other obstructions, and to meet an ascending stream of chlorine gas. The reaction,



takes place and the liberated bromine vapors are allowed to escape through the top of the apparatus into a suitable condenser. The same principle, with slight modification, is employed for the preparation of iodine from kelp. The impure iodine is purified by sublimation.

The preparation of iodine from the sodium iodate,  $\text{NaIO}_3$ , in Chile saltpeter involves a more complex method of manufacture. The mother liquors remaining after the nitrates are largely removed by crystallization are treated with sodium bisulfite,  $\text{NaHSO}_3$ , and the following reaction takes place:



The solid iodine is allowed to settle and is washed and pressed into blocks and after drying is **sublimed**. Sublimation is a term used to describe the change of a substance from the solid to the gaseous state or from the gaseous to the solid form without the intermediate liquid form being produced. The process is not at all uncommon. Frost and snow are sublimed forms of water. Sulfur and many other substances condense directly from gaseous to solid form when the gases encounter cold surfaces. The process is frequently employed for purifications.

**Physical and Chemical Properties.**—A table of properties of the halogens is here given and some of its more important features will be discussed in the text.

Elementary formula...	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
Atomic weight.....	19	35.45	79.92	126.92
State at room temperature	} Gas	Gas	Liquid	Solid
Color.....	} Light yellow	Greenish yellow	{ Reddish brown (vapor red)	Grayish black (vapor violet)
Boiling point.....	-186°	-33.6°	50°	184°
Specific gravity of vapor	} 1.31	2.51	{ Liquid at 0° 3.1883 Gas 5.52	Solid 4.93 Gas 8.72
Freezing point.....	-223°	-102.0°	7.3°	114°
Order of activity with hydrogen	} 1	2	3	4
Specific heat.....	++	++	{ Solid 0.08432 Liquid 0.1071 }	0.05412
Solubility at 0° C. in 100 cc. of water	} Interacts	1.49 g.	4.3 g.	0.32 g.
Hydrate.....	No hydrate	Cl <sub>2</sub> ·8H <sub>2</sub> O	Br <sub>2</sub> ·10H <sub>2</sub> O	No hydrate

The extreme chemical activity of fluorine renders the determination of its density difficult, but apparently the molecular weight is 38. The corresponding value for bromine, when its density is measured at a temperature below 750° C., is 160 and for iodine is 254.8. These values, like that for chlorine, indicate an atomic complexity of the molecules of two. If, however, the iodine and bromine vapors are heated above 750 degrees they expand more rapidly than accords with Charles' law and the density diminishes; so that at 1050° C., the density of bromine corresponds to a molecular weight of 150.5 and that of iodine at 1700° C. has fallen to 127. This is taken to mean that both bromine and iodine molecules, the latter more readily, are broken down by increase of temperature into simpler molecules of one atom each. A table for the dissociation values of iodine is appended.

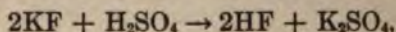
Temperature.....	480°	855°	1043°	1275°	1390°	1468°
Specific gravity of vapor.....	8.74	8.07	7.01	5.82	5.27	5.06
Dissociation, percentage.....	0	8.6	25	50.5	66.2	73.1

The same dissociation takes place with chlorine, but less markedly. Thus the density, compared with hydrogen = 2, is but 47.3 at 1200° C., while at 600° C. it is 70.92. Vapor density measurements of fluorine at high temperatures have not been made.

It will be noted in the table that the atomic weights of these elements are fluorine = 19, chlorine 35.45, bromine 79.92, and iodine



126.92. These values represent the accepted values of the least weight of these elements contained in a gram molecular weight of any of their volatile compounds. Of course, no one determination gives these values and the number used as the unit combining weight may be and sometimes is determined indirectly. For example, the atomic weight of fluorine was determined by Dumas (1860) as follows: Pure potassium fluoride treated with sulfuric acid yields potassium sulfate in the ratio of 1 : 1.4991. We have then



and if we use the atomic weight for potassium 39.1 and for sulfur and oxygen 32.07 and 16, respectively, we have the equation

$$2(39.1 + x) : (2 \times 39.1) + 32.07 + (4 \times 16) : 1 : 1.4991,$$

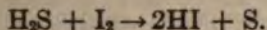
and if we solve for  $x$  we have  $x = 19$ . Even if no volatile compound of fluorine were known, this would be taken as its atomic weight and no volatile compound is known requiring the adoption of a lesser value.

The four elements present a series showing increasing color and decreasing chemical activity, with increase of atomic weight. That such related properties are the rule among elements of like chemical properties will appear when the generalization known as the periodic law is presented.

In the preceding discussion it should be apparent to the reader that since these elements all form salts with sodium similar to common salt, a general resemblance in chemical behavior is to be expected. Such is indeed the case. Like chlorine, all the elements unite with hydrogen and the metals to form compounds, known as the halides, in which the halogen acts as a univalent element. Also all of them unite with many non-metals to form halides which, like the non-metallic chlorides, are decomposed by water to form two acids. The order of activity in these respects is the inverse of that of the atomic weights, iodine being, for a given concentration, least active (see also the halogen acids). We do not have the same beautiful symmetry when we consider their union with water. Bromine, it is true, unites with water to form an unstable hydrate,  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ , but fluorine decomposes water, even in the dark, and iodine furnishes no indication of the formation of a hydrate.

Each of the elements is able to act on compounds by displacement and a study of their relation in this respect is both very interesting and instructive. If hydrogen sulfide is passed into water

containing iodine (see laboratory experiment) the following reaction takes place:



The same reaction takes place with any of the other halogens and indeed with increasing vigor as the atomic weight is less. In turn, if an iodide is treated with bromine the reaction,  $2\text{KI} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$ , takes place, and, in turn, bromine is displaced by chlorine and chlorine by fluorine. The same order of activity manifests itself in the behavior of the elements as substituents for hydrogen in water, iodine being so relatively inactive that it reacts with water,  $2\text{H}_2\text{O} + 2\text{I}_2 \rightarrow 4\text{HI} + \text{O}_2$ , only when simultaneously some substance capable of utilizing the oxygen is present. (This is as ought to be expected from the law of equilibrium.)

The action of the elements upon the membranes of the eyes, throat and lungs places them in the same order. Doubtless were fluorine inhaled it would be more unpleasantly active than is chlorine. Bromine is ordinarily more unpleasant than chlorine, not by reason of its greater activity, but because being less volatile and also less rapid in its rate of diffusion (see law of diffusion) one may readily encounter it at a greater concentration than the more active chlorine.

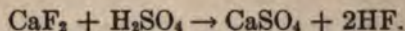
**Uses of Halogens.** — Fluorine as such naturally has no practical applications. Bromine finds application in a variety of ways in metallurgy and photography and particularly in chemical industries, such as dye manufacture; but as a disinfectant and oxidizing agent its use is limited in favor of the cheaper chlorine.

Iodine, on the other hand, in spite of its high cost, finds extensive application in the manufacture of photographic plates, in medicine as a lotion, in dye manufacture, and the preparation of the numerous iodides used in medical practice, *e.g.*, iodoform. It also is a very valuable laboratory reagent, being used in the quantitative estimation of many substances.

**The Hydrogen Halides.** — The halide compounds of hydrogen are both important and interesting. They may be formed in all the ways discussed under hydrogen chloride and yet the modifications needed in their preparation and the variation in their properties is very illuminating. All are colorless gases, very soluble in water and, therefore, fuming strongly in air. Hydrofluoric acid may be made by direct union of hydrogen and fluorine, the

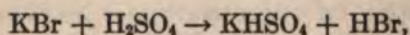


rate of reaction being so rapid, even in the dark, that it is of explosive violence. The acid may also be made by hydrolysis of non-metallic fluorides, *e.g.*,  $\text{SiF}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{Si}(\text{OH})_4$ . (It is at the same time true that some hydrofluoric acid unites with silicon tetrafluoride to form a stable and soluble compound,  $\text{H}_2\text{SiF}_6$ , known as hydrofluosilicic acid.) Practically, however, the only method employed is the treatment of fluorides with a less volatile acid, *e.g.*,

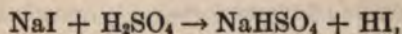


Since the hydrofluoric acid is capable of reacting with glass vessels (*vide infra*), the preparation must be carried on in metallic vessels, cast iron retorts and leaden condensers being usually employed. The solution of the acid is shipped and kept in lead, rubber or paraffin bottles.

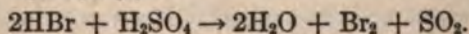
Hydrobromic and hydriodic acids may both be produced by the double decomposition of their salts with other acids. The conditions essential for completion of reversible reactions must be observed, *e.g.*, the acid used, if the halogen acids are volatilized, must be less volatile than they. Water in any considerable quantity must be absent, and yet good contact of the reacting substances must be secured. This is not possible except in a few cases. A further complication also arises. It will be recalled that hydrochloric acid can be oxidized, and chlorine produced, by good oxidizing agents. If we refer to sulfuric acid (*vide infra*), we see that in the concentrated state it is marked by its oxidizing capacity. If, then, we attempt to prepare hydriodic acid or hydrobromic acid by the most obvious method, treatment of the salts with sulfuric acid, we find that the fundamental reaction takes place as indicated:



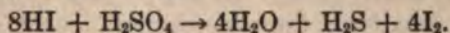
and



but the halogen acids are oxidized by sulfuric acid and the products are therefore impure, *e.g.*,



If hydriodic acid reacts with sulfuric acid, we get even more extensive reduction of the latter.



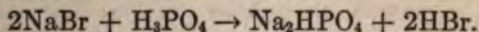
Such simultaneous occurrence of independent reactions is not

uncommon. The different reactions are very likely to be favored unequally by change of conditions. In the present case the higher the temperature employed the more rapid both sorts of reactions become; but the second sort, the reduction of the sulfuric acid, is the more increased, so that while at ordinary temperature some HBr and HI escape undecomposed, the proportion decreases as the temperature rises. At low temperatures the hydriodic acid may be but little more effective as a reducing agent than hydrobromic and hence not only may hydrogen sulfide be produced, but also sulfur dioxide and sulfur. We may have the following independent reactions which may be formulated as follows:

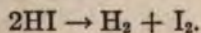
- (1)  $2\text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HI}$ .
- (2)  $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2$ .
- (3)  $6\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{H}_2\text{O} + \text{S} + 3\text{I}_2$ .
- (4)  $8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{H}_2\text{O} + \text{H}_2\text{S} + 4\text{I}_2$ .

It is possible, however, that reaction (3) may be absent, for if (2) and (4) are operative, sulfur may be produced by the reaction  $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 3\text{S}$ . (See properties of sulfur dioxide.) In any case the treatment of potassium iodide with concentrated acid may produce any or all of the products HI,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , S,  $\text{H}_2\text{O}$ ,  $\text{I}_2$ , and  $\text{K}_2\text{SO}_4$ . Whether the sulfate or acid sulfate is produced is a question of the temperature employed and of the amount of acid with relation to the salt used.

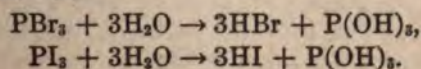
It is possible, of course, to produce the acids under consideration from their salts by double decomposition, using an acid not easily reduced, *e.g.*, phosphoric acid, the reaction being,



In this case, both by reason of the small solubility of the bromide, or iodide, in phosphoric acid and the relative inactivity (see Chap. IX) of phosphoric acid, the reaction is very slow and if the attempt is made to secure reasonable speed by rise of temperature, the acids decompose due to heat alone, as

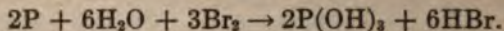


Hydriodic acid and hydrobromic acid may, however, be produced by the decomposition of non-metallic halides, even as is hydrochloric acid, *e.g.*,

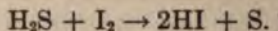




It is not essential to prepare the halides of the non-metal in advance, for they may be formed as used. If, for example, a mixture of phosphorus and water be treated with bromine we have



The most convenient method of preparation, however, is to make use of the displacing activity of the halogens, *e.g.*,



Other substances, as naphthalene,  $\text{C}_{10}\text{H}_8$ , benzene,  $\text{C}_6\text{H}_6$ , etc., may be used, especially with bromine, to produce hydrogen bromide.

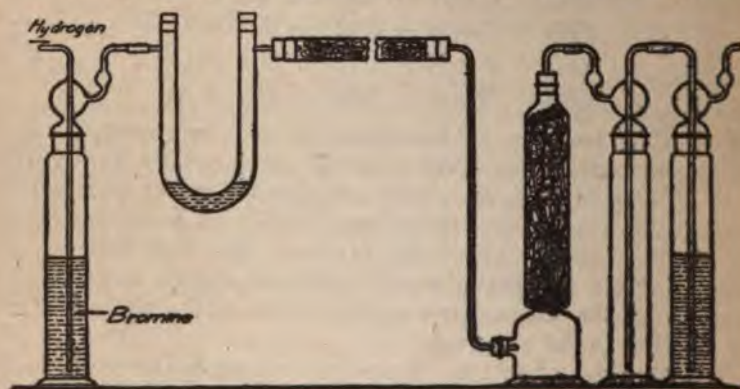
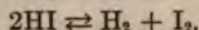


FIG. 39.

The question, of course, arises since we find fluorine and chlorine uniting with hydrogen to form the halides with explosive violence, the former spontaneously and the latter with the aid of the sunlight, can we not form hydrobromic and hydriodic acids also by direct union of the elements? The answer is in the affirmative. A study of the conditions involved in application of the method is extremely profitable. If bromine vapor and hydrogen are mixed, by allowing dry hydrogen to bubble through liquid bromine, the two gases unite, but do so much more slowly than is the case under corresponding conditions with chlorine and hydrogen. Even in the sunlight the reaction is not of explosive violence. If the mixture be ignited, or if it be passed over finely divided platinum, the reaction proceeds rapidly. An apparatus designed to illustrate the action is given in Fig. 39.

In the case of hydrogen and iodine, the activity of the iodine is so small that the rate of reaction is very slow. Yet if iodine vapor and hydrogen are passed over finely divided platinum or even through a hot tube, appreciable quantities of the iodide are produced, but the greater part of the iodine and hydrogen escape separately. If, however, we pass hydrogen iodide through a tube under like conditions, the same result follows, *i.e.*, some hydrogen and iodine are produced. When the reaction is conducted in a closed system, *e.g.*, a sealed tube at  $440^{\circ}$ , we find that whether we start with hydriodic acid or with a mixture of iodine and hydrogen in corresponding quantity the result is the same, *viz.*, 80% HI and 20%  $H_2$  and  $I_2$ . This is a typical example of a reversible reaction,



and it may be worth while to discover the relative speeds of the two reactions when equilibrium is reached. The speed of the reaction at any instant in the direction  $\rightarrow$  is  $K C_{HI}^2$ . The speed in the direction  $\leftarrow$  is  $K' C_{H_2} C_{I_2}$ , and therefore at equilibrium:

$$\frac{C_{H_2} C_{I_2}}{C_{HI}^2} = \frac{K'}{K} = K.$$

Substituting the values obtained for  $440^{\circ}$  C. we have,

$$\frac{10 \times 10}{6400} = \frac{1}{64} \quad \text{or} \quad C_{HI}^2 = 64 C_{H_2} C_{I_2}.$$

Therefore HI at unit concentration at  $440^{\circ}$  dissociates at  $\frac{1}{4}$  the rate at which iodine and hydrogen combine.

**Properties of the Halogen Acids.**—A table of the properties of the acids will be convenient for reference and may be followed by discussion of certain features.

	$H_2F_2$ , HF	HCl	HBr	HI
Molecular complexity.....	Gas	Gas	Gas	Gas
State at ordinary temperature.....	Gas	Gas	Gas	Gas
Boiling point.....	$19.5^{\circ}$	$-83^{\circ}$	$-68.5^{\circ}$	$-34^{\circ}$
Freezing point.....	$-92.3^{\circ}$	$-112^{\circ}$	$-86^{\circ}$	$-51^{\circ}$
Solubility, vol. to 1 of $H_2O$ .....	302 ( $H_2F_2$ )	525	600	425
Boiling point of solution.....	$111^{\circ}$	$110^{\circ}$	$126^{\circ}$	$127^{\circ}$
Composition of solution.....	43%	20.2%	48%	57%
Heat of formation, gaseous.....	38 Cal.	22 Cal.	8.1 Cal.	-6.1 Cal.
Heat of formation, liquid.....	49 Cal.	40 Cal.	26 Cal.	13.0 Cal.
Relative activity, approx.....	16	78	89	90



In several respects hydrofluoric acid offers variation from its related compounds to a degree not satisfactorily comparable with the atomic weight of fluorine. These variations may perhaps be ascribed to its molecular weight, which, if measured at  $0^\circ$  or in the neighborhood, has a value of 51 and decreases until about  $100^\circ$ . Its molecules are, therefore, polymerized and the formula may be  $H_3F_3$ , or  $H_2F_2$ , or mixtures of these with HF. Above  $100^\circ$  it consists, like the other hydrogen halides, of simple diatomic molecules. In aqueous solution the depression of the freezing point (*q.v.*) corresponds to the formula  $H_2F_2$ .

All the hydrogen halides, like other gases, liquefy if sufficiently cooled. The liquids, like the dry gases, are not acid in character. This phenomenon has been already met and requires explanation. A full discussion follows in Chapter IX. The absence of acid properties of the dry substances has led to the practice of distinguishing between the dry substances and their solutions in water by using the terms hydrogen fluoride, hydrogen chloride, etc., in speaking of the former. (See comment on page 126.) The dry substances, whether gaseous or liquid, are also non-conductors of the electric current, while their aqueous solutions and the solutions of their salts are excellent conductors. This difference also finds explanation in Chapter IX.

The heat of formation of the gases is a rough measure of their stability. The ease of decomposition is the inverse of stability and the table readily reveals why oxidation of the halide acids is more easily accomplished as the atomic weight of the halides

increases. The operation requires the expenditure of less energy.

An interesting illustration of van't Hoff's law of mobile equilibrium (*q.v.*) is furnished by hydrogen iodide. The proportion of hydrogen iodide decomposed when equilibrium is obtained in a homogeneous

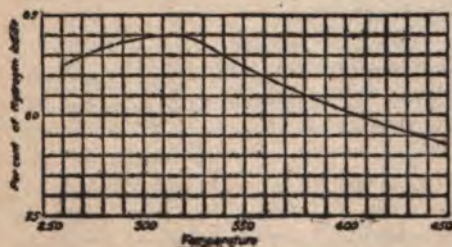


FIG. 40.

system decreases with rise of temperature until about  $320^\circ$  is reached, after which it increases. The heat of formation of HI at  $18^\circ$  is  $-6.1$  Cal. and at  $520^\circ$  it is  $+4.4$  Cal. The change of sign occurs at about  $320^\circ$ . The curve is shown in Fig. 40.

All the hydrogen halides fume strongly in moist air, due to their "combination" with water vapor (*cf.* p. 125). Solution in water takes place to an enormous extent; being greatest with hydrogen iodide, as respects weight, and with hydrogen bromide as respects volume. This solution is accompanied by marked rise of temperature (*cf.* heat of formation), by change in volume of the solutions, and by marked change in properties. The gases are liberated when the saturated solutions are boiled, but, unlike the gaseous solutions of hydrogen, oxygen, ammonia, etc., are not completely eliminated when the boiling point of water is reached. On the contrary, if dilute solutions are boiled, water is evaporated until a constant boiling mixture is obtained. Starting with a saturated solution, acid is expelled until the same boiling point and concentration is reached. For the different acids the concentrations and boiling points correspond to those given in the table.

In spite of these strong indications of chemical union between water and the hydrogen halides, the orthodox chemist looks upon the solutions as mixtures rather than compounds, because, in part, the properties of the solutions vary continuously within wide limits of concentration. Further, the solutions, if cooled, at various dilutions, give hydrates corresponding more or less satisfactorily to the formulas, for hydrochloric acid,  $\text{HCl} \cdot 3\text{H}_2\text{O}$ ;  $\text{HCl} \cdot 2\text{H}_2\text{O}$ ;  $\text{HCl} \cdot \text{H}_2\text{O}$  but none corresponding to the formula  $\text{HCl} \cdot 8\text{H}_2\text{O}$ . (See phase rule.) Somewhat similar hydrates of the other acids have been made.

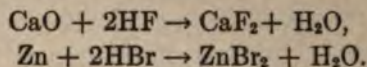
In truth, it seems to the writer that it were the part of wisdom, as well as good pedagogy, to admit that at present we are not able satisfactorily to assign the hydrogen halides in aqueous solution to either category, compound or mixture. They furnish one of the "missing links" between compounds and mixtures.

**Uses of the Acids.**—Hydrofluoric acid finds its most extensive application in the arts by reason of the fact that it reacts with silica and silicates to form a volatile compound. Thus,  $\text{CaSiO}_3 + 6\text{HF} \rightarrow \text{CaF}_2 + \text{SiF}_4 + 3\text{H}_2\text{O}$ . This reaction is applied to etching glass for various purposes, such as graduations on thermometers, hydrometers, volumetric vessels, etc. The strong solution, as well as the gas, is a very poisonous substance, and at least one tragedy (the death of the chemist, J. Nickles) and many painful burns are to be laid at its door.

Hydrobromic acid and hydriodic acid, probably by reason of their relatively high cost, find little application in the arts.



**Salts.** — The compounds formed by union of the halides with metals are called salts of the acids, because, however they are actually made, they may be regarded as produced by the action of the acids upon metals, oxides or hydroxides, as illustrated by the equations:



These compounds are very extensively used in various ways, but the necessity of putting more general principles at the command of the reader as expeditiously as may be, renders it advisable to postpone the discussion until the metal involved is also under discussion.

**Exercises.** — 1. If iodine is impure, what impurities is it likely to contain? If heated with KI what is the result and what is this process of purification called?

2. How would you undertake to prepare pure samples of hydrofluoric, hydrobromic and hydriodic acid?

3. Which methods, other than electrolysis, used for the preparation of iodine are ineffective for fluorine? Discuss each method in detail.

4. When sodium chloride, sodium bromide, and sodium iodide are heated separately, explain what happens and the differences. Illustrate as fully as possible by equations.

5. If hydriodic acid were being formed by interaction of sodium iodide and sulfuric acid, explain how the reaction could be made slower, stopped or reversed without separation of the components.

6. If the specific gravity of a given sample of bromine vapor is 5.2, what is the percentage of  $\text{Br}_2$  and Br molecules present?

7. Calculate the degree of dissociation of iodine molecules when the specific gravity of the vapor is 6.0.

8. Look up the heat of formation of the halides of hydrogen and place the halogens in the order of speed with which they would react as substitutes for hydrogen in hydrogen compounds.

9. Explain why all the hydrogen halides "fume" in moist air.

10. Explain the existence of acid fluorides. What is the most reasonable explanation of the heat of solution of the hydrogen halides?

11. Make a list of the uses to which each of the elements and hydrogen halides discussed in this chapter is put.

## CHAPTER IX

### OSMOTIC PRESSURE AND IONIZATION

If any soluble substance be placed at the bottom of a cylinder and water poured upon it, gradually the solvent will take up the substance and, in the course of time, the solute will be found distributed throughout the solvent. This action is analogous to that which occurs when two gases, not chemically reactive with each other, are allowed to come into contact. Just as the gaseous intermingling may be ascribed to an automatic process called diffusion, so the process of solution may be ascribed to the automatic motion of the molecules of the solvent and solute, and a special name applied to the process. The name used for the process is osmosis (from  $\acute{\omega}\sigma\mu\acute{o}\varsigma$  = a push) and the force assumed as the cause of the motion is called osmotic force. Also, just as in the case of diffusion by introducing a porous partition between gases it is possible to show that diffusion may produce an increase of pressure on one side of the partition, so by introduction of a suitable partition between the solvent and the solute it is possible to produce a pressure on one side or the other of the membrane. For example, if a carrot be scraped to remove the outer cover and a hole be bored in the top, filled with sugar, and stoppered securely with a rubber cork carrying a glass tube, and the whole immersed in water, the water will pass into the sugar and the solution will rise in the tube to a height which produces a sufficient pressure to stop the process. (Fig. 41.) The pressure so produced is known as "osmotic pressure." Of course, with a fragile wall like that of a carrot it is not possible to secure an accurate measure of this pressure, which is very great as will appear in the sequel (*cf.* p. 159). If, however, a very strong wall is prepared by depositing a membrane of copper ferrocyanide in the walls of a clay cup, we may secure a membrane capable of resisting the pressure, and which at the same time seems almost impervious to the sugar solution. Figure 42 shows an osmotic pressure apparatus. The membrane is deposited in the walls of the cup. Such membranes



as the carrot cell-walls and the copper ferrocyanide membrane are called semipermeable, because they will permit free passage of a solvent and prevent the reverse passage of the solution.



FIG. 41.



FIG. 42.



FIG. 43.

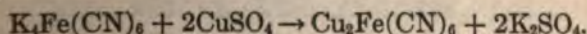
membranes, more or less perfect, are very common among organic compounds; for example, eggs are surrounded by a membrane within the shell which freely permits the ingress or egress of water, but prevents the simultaneous passage of the contents.

g contents. Other examples are furnished by the living cells of plants, such as root hairs, leaf cells, etc., and by animal membranes, such as the bladder, kidneys, periosteum, intestines, etc. Many of the processes involved in animal and plant metabolism and anabolism involve osmotic phenomena. Examples of semipermeable membranes are rare among simple compounds, though not so uncommon as is ordinarily supposed. Water itself acts in this manner if it be placed in a thin layer between chloroform and ether, as shown in Fig. 43.

The reader is asked to recall that any two substances may bear the relation of solvent and solute, and to observe that very rarely is there to be obtained an approximately perfect membrane. By "perfect membrane" is meant such an one as will permit the transmission of one component, usually called the solvent, and wholly prevent the passage of both solute and solution.

**History.** — The history of the study of osmotic processes is very extensive and is linked with some of the most important developments of chemistry. The literature is enormous and the present discussion must be confined to only the more striking points. The phenomenon was first observed by Abbé Nollet (*Mem. de l'Acad. Roy. d'Sciences*, pp. 57-104) in 1748, but was forgotten and rediscovered by Sömmerring, in 1814. In 1855, Hermite (*Ann. de Chimie et de Physique* (3), 43, 420-431) showed the semipermeability of water between ether and chloroform, and of castor oil between water and alcohol, etc. The first important step toward exact measurement was made in 1867, when Traube (*Archive f. Anatomie und Physiologie*, 1867, p. 87) discovered the semipermeability of copper ferrocyanide and similar precipitated membranes.

In 1877, the Dutch botanist, Pfeffer (*Osmotische Untersuchungen*, Leipzig, 1877) precipitated such membranes in the pores of clay cups by filling them with copper sulfate and placing them in a solution of potassium ferrocyanide. Where the solutions met within the cup a thin film was deposited, as shown by the following equation:



The ferrocyanide of copper being insoluble, the other components were washed out by water and the cup used to measure quantitative values of the osmotic pressures produced by water with various solutes. From Pfeffer's results, van't Hoff, in 1886 (*Zeit. für Phys. Chem.*, Vol. I, p. 1) calculated the values for



molar solutions and deduced his theory of solution (*vide infra*). In 1887, from Pfeffer's results and the phenomena of freezing and boiling points and the conductivity of certain solutions, Arrhenius deduced the ionization hypothesis (*vide infra*).

In the period between 1901 and 1911, Morse and co-workers, (Am. Chem. Jour., Vols. 25, 28, 29, 34, 36, 37, 38, 39, 40, 41, 42, 43) and the Earl of Berkeley (Trans. Roy. Soc., Vols. 206 and 209, and Proc. Roy. Soc., Vols. 73, 77, and 82, 1904-1909) made exact measurements of osmotic pressures and established the quantitative relations on which the following discussions are based. In 1907, L. Kahlenberg (Jour. Phys. Chem., Vol. 7) published an investigation designed to demonstrate the identity of osmotic force with the ordinary conception of chemical affinity and presented conclusions strongly at variance with what may be considered the orthodox view.

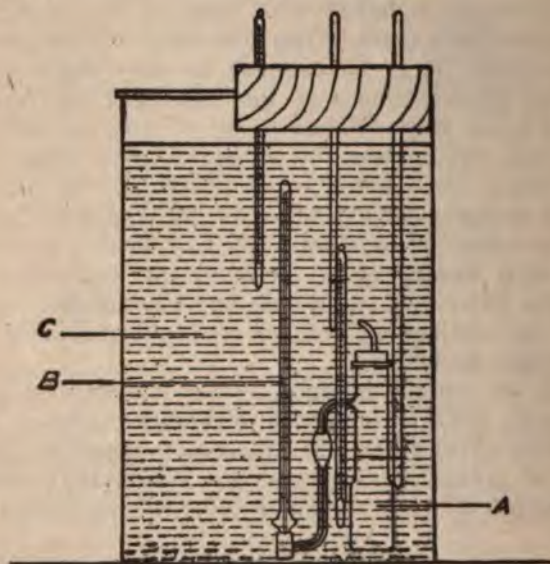


FIG. 44.

**Osmotic Pressures and Boyle's Law.**—The type of apparatus suitable for exact measurement of osmotic pressure is illustrated by Fig. 44. *A* is a porous cup which contains the solution; *B*, a manometer for measuring the pressure. The whole apparatus is

immersed in a thermostat,  $C$ , so that a constant temperature may be had. With such an apparatus, using copper ferrocyanide as a membrane, deposited in specially prepared porous cups by electrolysis, Morse obtained the following results with cane sugar solutions and water at  $0^{\circ}$  Centigrade:

I.	II.	III.	I.	II.	III.
Concentration weight molar.	Osmotic pressure in atmospheres.	Gas pressure in atmospheres.	Concentration weight molar.	Osmotic pressure in atmospheres.	Gas pressure in atmospheres.
0.1	2.42	2.24	0.6	14.12	13.44
0.2	4.79	4.48	0.7	16.68	15.68
0.3	7.00	6.72	0.8	19.15	17.92
0.4	9.35	8.96	0.9	21.89	20.16
0.5	11.75	11.20	1.0	22.45	22.40

It will be observed that the osmotic pressure increases with the concentration of the solution, and if we should represent the change

of pressure with change of concentration by means of a graph, as in Fig. 45, we get the curve represented by the solid line. If we assume that the sugar could be converted into a gas, and that it would under such conditions conform exactly with Boyle's law, we should get the values for gaseous pressure, shown in column III of the table and also shown by the dotted line. Results of similar type can be obtained for other solutes, but, unfortunately, while the general course is similar, the exact values are difficult to obtain.

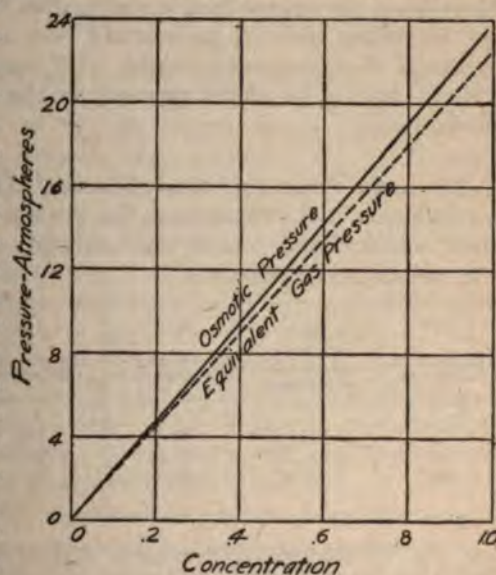


FIG. 45.

Most semipermeable membranes permit a flow of solution in the direction opposite to that of the pure solvent and hence the results



obtained are the difference between the opposed tendencies. The relation is, however, sufficiently close, so that, taking the known sources of error into account, even with the less accurate data secured by Pfeffer, van't Hoff expressed the result in a form to show the relation between Boyle's law for gases and osmotic pressure, *viz.*, **The pressure caused by osmosis varies directly as the concentration.** The experimental verification of this law, if it be a law, is as yet impossible because of various factors, aside from imperfectly semipermeable membranes, the extent of the effects of which are at present undetermined. Among these factors may be mentioned change of concentration, due to formation of hydrates (see Jones' Solvate Theory), the molecular attraction of dissolved molecules and the volume of the molecules themselves. Assuming the rule to hold, however, we realize that we are here dealing with a tendency capable of operating in the face of strong opposition. For example, if it holds, a molar solution of a compound may attract moisture through a membrane so powerfully that a pressure approximating 360 pounds per square inch is required to prevent the process. We are, therefore, able to understand how moisture travels through tree cells to any needed height. (It may be said that botanists are not agreed to admit osmosis as the *sole* explanation of sap movements.)

**Osmotic Pressures and Charles' Law.**—Morse also gives the following data concerning the change of osmotic pressure of a sugar solution with temperature change. The concentration used is a volume molar solution.\*

I. Temperature, Centigrade.	II. Osmotic pressure in atmospheres.	III. Gas pressure in atmospheres.	I. Temperature, Centigrade.	II. Osmotic pressure in atmospheres.	III. Gas pressure in atmospheres.
0°	24.45	22.4	15°	25.42	23.6
5°	24.53	22.8	20°	26.12	24.1
10°	25.06	23.2	25°	26.33	24.5

\* By "volume molar" solution is meant the concentration in gram molecular weights per liter of solution; by "weight molar" is meant the concentration in gram molecular weights per liter of solvent. It will be noted below (see p. 161), that the exact correspondence between gaseous pressure and osmotic pressure only obtains with weight molar solutions; hence the lack of coincidence of the nearly parallel lines in Fig. 46.

The values in Column III are calculated on the assumption that a gram molar weight of sugar would in a volume of 1 liter exert a pressure of 22.4 atmospheres and with increase of temperature would act in accordance with Charles' law. If we plot these values we get a graph of the type given in Fig. 46. Consequently, with the same reservation as regards confirmation by experiment and factors modifying accuracy of measurement, we may say that osmotic pressure is proportional to the absolute temperature, concentration remaining constant.

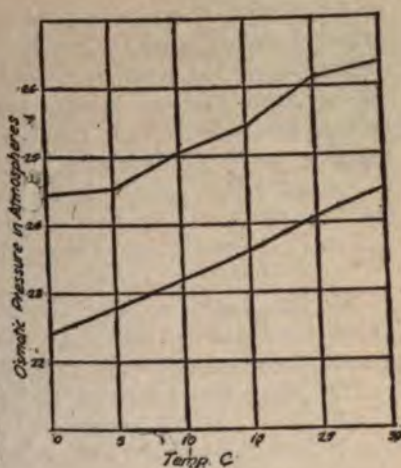


FIG. 46.

**Avogadro's Hypothesis.**—In a similar manner it is satisfactorily demonstrated, so far as exact demonstration is possible, that gram molecular weights of various solutes exert equal osmotic pressure at equal concentration. For example, 342 g. of sugar in one liter of water was shown by Morse (Am. Chem. Jour., Vol. 34, p. 85) to have an osmotic pressure of 22.610 atmospheres. Were the sugar a gas confined to one liter volume, according to Avogadro's hypothesis, the pressure should be approximately 22.4 atmospheres. If this relation holds, it should be possible to determine the molecular weights of substances in solution. That it is not so used is due to the experimental difficulties of exact measurement and to the fact that it can be shown that changes of freezing point and of boiling point with change of concentration are, *mutatis mutandis*, of the same value, and these are more readily available as means of measurement.

**Van't Hoff's Solution Hypothesis.**—From the striking analogy between the gas laws and osmotic pressure, van't Hoff reached the conclusion that, as later modified by Morse, substances in solution behave as we should expect were they gaseous and confined to the volume of the solvent in the pure state. This



assumes that "osmotic pressure and related properties, vapor pressure, freezing point, and boiling point — of dilute solutions — depend upon the number of molecules of solute in unit volume of the solution and are independent of the chemical nature of the solvent and solute and of the relations between solvent and solute." (Mellor, p. 210.) This view of the nature of solutions is perhaps to be described as the orthodox of chemists at present, but is far from satisfactory, and a brief discussion of its shortcomings will be presented later. (See p. 186.)

***Modifications of the Gas Laws for Osmotic Pressure.***—

There are three classes of exceptions to the previously discussed generalizations for osmotic pressure:

- (1) The generalizations fail to hold for concentrated solutions.
- (2) They do not correspond to the facts for any acid, base, or salt in solution in water, in which cases the osmotic pressures observed are always in excess of the values to be expected from the generalizations.
- (3) The osmotic pressure of solutions is occasionally less than that calculated for solutions of corresponding concentration. These variations of fact from the generalizations and the hypothesis deduced from them would ordinarily be sufficient to wholly discredit them, and would in all probability do so in this instance, were not plausible and more or less satisfactory explanations of all the variations at hand. These will be given after the related phenomena are discussed.

***Freezing Point of Solutions.***—When a foreign substance is dissolved in a liquid the freezing point of the solution is lower than that of the pure solvent and for moderate concentrations the lowering is proportional to the concentration. This fact was clearly demonstrated by Blagden (Phil. Trans., 78, 277 (1788)), but his discovery was neglected for nearly a hundred years until rediscovered by Rüdorff (Pogg. Ann., 114, 63). In 1882, Raoult (Compt. Rend., 94, 1517, and 95, pp. 188 and 1030), using solvents other than water and water solutions of many organic substances, demonstrated that equimolecular concentrations lower the freezing point of a given solvent to the same extent, *e.g.*, 342 grams of sugar and 32.03 grams of methyl alcohol each lower the freezing point of an aqueous molar solution 1.89° C. Equimolecular amounts of many other substances produce the same lowering

the freezing point of aqueous solution. The quantity,  $1.89^{\circ}\text{C}$ ., known as the gram molecular lowering of the freezing point of water and so long as the above statements hold it is obvious to determine the molecular weight of a substance it is simply necessary to determine the quantity of material required to lower the freezing point of water  $1.89^{\circ}\text{C}$ .

The method is extensively employed and the most frequently used device is suggested by Beckman (*Zeit. für Phys. Chem.*, 2, p. 323 and p. 638). (See Fig. 47.) The apparatus consists of a tube with a neck, *A*; a surrounding jacket, *B*, to prevent local over-cooling; a bath of ice salt with a stirrer, *C*, to prevent one portion of the solution being frozen too quickly; and a very delicate thermometer. The details of the operations are given in laboratory manuals. (See also texts on physical chemistry.)

The weight of the substance per liter  $w$  and the molecular weight  $M$  as  $f$ , the lowering of the freezing point, is to  $1.89$ , or,

$$M = 1.89 \times w/f.$$

Of course when 1000 grams of water is not used (it is a needlessly large quantity), it is necessary to multiply the quantity of the substance by the value  $1000/w'$ , where  $w'$  is the actual weight of water used. The whole expression may then be written  $M = 1.89 \times w/f \times 1000/w'$ , where  $w$  = the actual weight of solute dissolved in  $w'$  grams of solvent.

Each solvent has a molecular depression peculiar to itself and in order to find the molecular weight of substances using a given solvent it is first necessary to find the molecular lowering, using substances of known molecular weight. This value is for benzene  $1.86^{\circ}$ , for acetic acid  $3.89^{\circ}$ , for phenol  $7.6^{\circ}$ , mercury  $42.5^{\circ}$ , naphthalene etc. (For a gram molecular weight of solute per 1000 grams of solvent.) Using any of these solvents, it is only necessary to substitute in the above formula the molecular lowering of the given solvent.

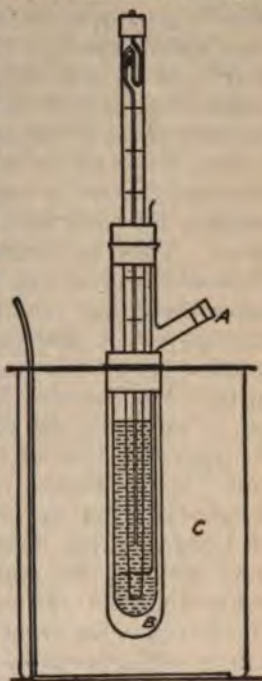


FIG. 47.



The normal mode of behavior of the freezing point of solutions is subject to the same variations as were noted in the case of osmotic pressures (cf. p. 162). Raoult's Law does not rigidly express the behavior of concentrated solutions (cf. p. 166). Many substances give larger molecular weight values by the freezing point method than are obtained by other methods. For example, the molecular weight of alcohol vapor is 46 (*i.e.*, Sp. gr.  $\times 28.95 = 46$ ). This weight corresponds to the formula  $C_2H_5OH$ . The lowering of the freezing point of benzene by alcohol is but half what we should expect, *viz.*,  $2.45^\circ$  for a molar solution. This sort of variation from expected values is called **abnormal**. The hypothesis offered to account for such variations is that association of molecules takes place. Thus, in benzene solution we have  $2C_2H_5OH \rightarrow (C_2H_5OH)_2$ . It would lead us too far to discuss the reasons for making this assumption, but analogous association of molecules is frequently encountered in gases and hence the assumption of association in solution is not unreasonable. For example, we know that iodine at high temperature,  $I$ , becomes  $I_2$  at lower temperatures,  $2I \rightleftharpoons I_2$  (cf. p. 145), and also  $2NO_2 \rightleftharpoons N_2O_4$  (cf. p. 294).

The third type of variation, also called **abnormal**, is more difficult. If we dissolve acids, bases, or salts of known molecular weights in water, the lowering of the freezing point is larger than is to be expected from Raoult's law. Thus, a normal solution of common salt, *i.e.*, 58.5 grams per liter, lowers the freezing point  $3.46^\circ$  instead of  $1.89^\circ$ . All other solutions of acids, bases or salts show a similar variation from normal behavior. The quantitative variation is not identical for different substances. In view of such variations the student has a perfect right to question seriously the validity of Raoult's Law as applied to aqueous solutions. He is asked, however, to remember that Avogadro's hypothesis was at first rejected, largely because using it as a basis of calculation certain substances appeared to have impossible molecular weights. Thus, ammonium chloride,  $NH_4Cl$ , formed by the direct addition of ammonia,  $NH_3$ , and hydrochloric acid,  $HCl$ , must have a molecular weight of 53.5. The specific gravity of its vapor multiplied by 28.955 (see p. 100) gives values ranging all the way from nearly 26.5 to approximately 53 according to the conditions under which the specific gravity is determined.

It finally was realized that it was more reasonable to assume that ammonium chloride dissociates when converted to a vapor, *i.e.*,  $NH_4Cl \rightleftharpoons NH_3 + HCl$ , than to reject the very useful hypothesis

of Avogadro. In a similar manner we may find that it is better and more reasonable to seek an explanation of excessively large depressions of the freezing point than to reject the generalization of Raoult. This explanation is found in the hypothesis of Arrhenius (p. 171).

**Boiling Point of Solutions.**—We have already pointed out that the boiling point of a liquid is the temperature at which its vapor tension equals the gaseous pressure upon it. In 1832, Faraday (Ann. Chem. et. de Phys., vol. 20, p. 324) attempted to determine the exact influence of dissolved substances upon the boiling point of water but was unable to secure concordant data. In 1858, Wüllner pointed out that the lowering of the vapor pressure of a solution, therefore the elevation of the boiling point, is proportional to the concentration of the dissolved substance, provided the dissolved substance is not volatile. In 1882, Raoult showed that in a non-aqueous solvent equimolecular concentrations of dissolved substances cause equal elevations of the boiling point. Even with water the rule holds good for solutes such as sugar, alcohol, ethyl acetate, etc. The rise in the boiling point for one gram-molecule

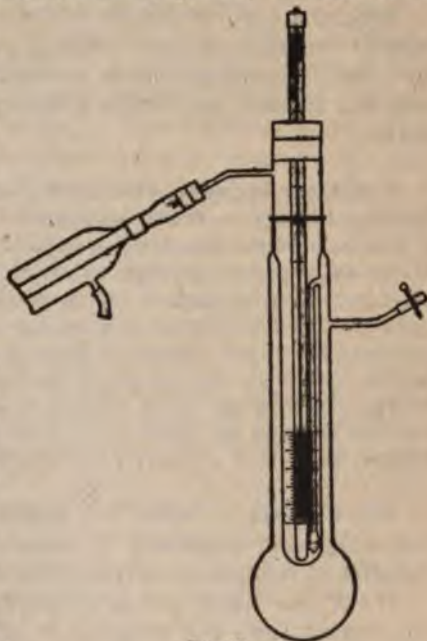


FIG. 48.

of solute per 1000 grams of solvent is for water  $0.52^{\circ}$ ; for acetone,  $1.67^{\circ}$ ; for benzene,  $2.67^{\circ}$ ; for ether,  $2.16^{\circ}$ ; for carbon disulfide,  $2.6^{\circ}$ . The apparatus for measuring boiling point changes is usually a more or less modified variation of an apparatus first suggested by Beckman in 1889. The form shown in Fig. 48 is known as McCoy's apparatus. (For other variations consult texts on Physical Chemistry.) It will be clear from the considerations cited under the topic of freezing points that this method may also be used for molec-



ular weight determination, provided substances of known molecular weight are used to determine the molecular elevation, by using the proportion  $\text{mol. wt.} = 0.52 \times w/f \times 1000/W$ , where 0.52 is the molecular elevation,  $w$  = weight of solute,  $W$  = weight of solvent and  $f$  the elevation of the boiling point.

It is to be emphasized that the three modifications of the above statements must be made as in the case of the freezing points. The rules fail to hold for concentrated solutions, and if we assume that they hold at all we must also assume in some cases dissociation and in others association of molecules.

Special attention should be drawn to the fact that the general laws of osmotic pressure, freezing point and boiling point do not hold with substances which are capable of interacting chemically with the solvent, *e.g.*, sulfur trioxide, nitrogen peroxide, etc., with water.

**Relation between Osmotic Pressure, Freezing Points and Boiling Points.** — It may be pointed out that in each of the three classes of phenomena under consideration we are dealing with the same sort of change. In the case of osmotic pressure, we are measuring the pressure which develops when the attempt is made to prevent a solution from becoming more dilute by contact with a pure solvent. In the case of boiling or freezing points, we are measuring the energy required to separate water from solution. Indeed, it is possible to calculate the lowering of the freezing point and the elevation of the boiling point from the values obtained in the general gas equation and the latent heat of fusion and latent heat of vaporization. (See General Discussion — Bigelow, *Theoretical Chemistry*, pp. 328-329.)

**Electrolysis.** — When the terminals from a source of current electricity are connected by means of various materials, three varieties of substances may be speedily distinguished:

(1) Those which act as insulators and prevent the passage of the current from one terminal to another. The vast majority of substances belong to this class, *e.g.*, nearly all pure liquids, including water; the non-metallic elements in general and most dry compounds. These are called non-conductors.

(2) Those which permit the passage of the current, but which remain essentially unchanged while the current passes and wholly unchanged when the source of the current is removed. These are for the most part metals and their alloys. These are called **conductors of the first class**.

(3) Those which allow the passage of the current, but are

ultaneously decomposed by the current or cause decomposition at the terminals and hence suffer change in composition. The substances belonging to this class are acids, bases or salts in solution in water or when highly heated. These substances are known as **conductors of the second class, or electrolytes**. The process of transfer of electricity through electrolytes is called electrolysis and is the subject of the present discussion.

**History.**—The process of electrolysis was first noted by Nicholson and Carlisle in 1800, when they observed the decomposition of pure water placed between the poles of a voltaic pile (the first known source of current electricity, consisting of alternate plates of silver and copper between layers of cloth saturated with salt solution, invented in 1799 by Volta). This discovery was quickly followed by a series of discoveries, notably those of Berzelius (1803), that by passage of current through salt solutions and of gases in water the "combustible constituents of alkalies and of earths separated themselves at the negative pole of the battery and that oxygen acids and oxidized substances separated at the other." This was followed in 1806 by the strikingly interesting series of investigations by Davy, which culminated in his isolation of potassium and sodium by the electrolysis of their fused hydroxides. In 1834, *et seq.*, Faraday showed that the quantity of substances decomposed is exactly proportionate to the quantity of electricity which has passed through the electrolyte, and that if the same current be led through a series of electrolytes the quantities of the various materials liberated at the poles is proportionate to their chemical equivalents. These two statements are known as Faraday's laws. An illustration of the latter is furnished by passing a current through a series of cells, containing the following solutions in water:  $\text{H}_2\text{SO}_4$ ,  $\text{CuCl}_2$ ,  $\text{AgNO}_3$ ,  $\text{AuCl}_3$  and  $\text{SnCl}_4$ . (See Fig. 49.) The following relative amounts are liberated at the negative poles: Let the amount of hydrogen be one, then  $\text{H} = 1$ ;  $\text{O} = 108$ ;  $\text{Cu} = 31.8$ ;  $\text{Au} = 65.7$ ;  $\text{Ag} = 29.8$ . These are the relative equivalent weights of the metals. Faraday also invented

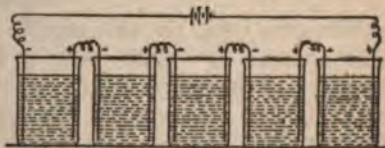


FIG. 49.

the extremely interesting nomenclature which we still employ. The word electrolyte (from  $\eta\lambdaεκτρον$  = amber, representing elec-



tricity, and λύσις = solution) was designed to describe a solution which acts as a conductor of the second class; and by usage has also come to mean a substance which, when added to a solvent, forms such a conductor. Electrolysis (ἤλεκτρον and λύειν = to loose) is the process of decomposition by means of the current. To more accurately describe the details of the process Faraday also proposed to call the terminals, at which the current enters and leaves the solution, the electrodes (from ὁδός = road or path) and to distinguish them by prefixes (κατά = downward and ἀνά = upward); the electrode at which the positive elements appeared is called the **kathode**, or **cathode**, and the non-metallic elements, or radicals, appeared at the **anode**. The apparent effect of the passage of a current is to cause a decomposition of the solute into two sorts of material, one sort eventually appearing at the anode and another at the cathode, and they may be considered, therefore, as traveling through the solution hence are called ions (from ἰόν = a traveler) and, respectively, cations and anions.

**The Process of Electrolysis.**—If a solution of copper sulfate be placed between two platinum electrodes (see Fig. 50), which are kept at a definite potential or "charge" from some source of current, a dynamo or storage battery, the visible process that goes on is the deposition of copper at the negatively-charged electrode, the cathode, and a liberation of oxygen at the anode. On careful examination of the liquid around the anode it may be shown that sulfuric acid is accumulating there and, of course, diffusing thence throughout the liquid. If the operation be continued

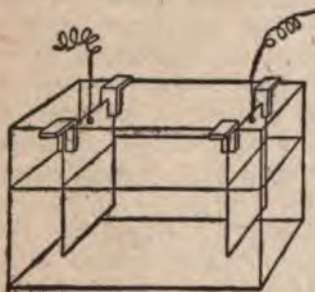
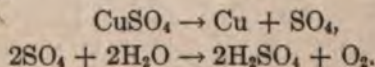


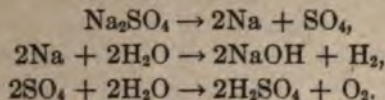
FIG. 50.

sufficiently long, all the copper will be deposited and an equivalent amount of oxygen will be liberated. We may express these changes as follows:



If instead of copper sulfate we use silver nitrate, we get a deposit of silver at the cathode, and liberation of oxygen and formation of nitric acid at the anode. If we use a sodium or potassium

salt instead of one of the less chemically active metals, we get an additional reaction. Thus from sodium sulfate:



It does not always follow that the anion decomposes the solvent, for if we use common salt or hydrochloric acid, of proper concentration, as a solute, we obtain a liberation of chlorine at the anode. All acids when electrolyzed liberate hydrogen at the cathode.

**Units of Measure of Electricity.**—It is perhaps desirable before taking up the explanations of electrolysis to discuss certain units of measure of electricity, which may or may not be familiar to the reader. The present two-fluid view of electricity dates from the time of Benjamin Franklin, who proposed the names positive and negative for the two sorts of electricity which are developed upon silk and glass by rubbing. These terms have been transferred to the kinds of "charge" developed at the opposite poles of a dynamo or of a voltaic cell. When these poles are connected by means of conductors, they are mutually discharged and a current is said to flow from one to the other. It is conventional to consider the direction of the flow as indicated in Fig. 51.

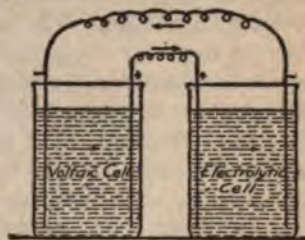


FIG. 51.

The elements or radicals which appear at the negative electrode are hence spoken of as positive and, conversely, those appearing at the positive pole are negative. The flow of a current through an electrolyte is, then, a mutual discharge of negative and positive ions (in the Faraday sense of the word) at the electrodes. The **units of measure** of this flow of current are derived by analogy with the flow of water from higher to lower levels. The unit **quantity** of electricity is called a coulomb and the chemical equivalent of this quantity is 0.001118 gram of silver, *i.e.*, one coulomb of electricity flowing through an electrolytic cell containing a silver salt will deposit 0.001118 gram of silver.



According to Faraday's laws, it will then take  $107.88/0.001118 = 96,493$  coulombs of electricity to deposit a gram equivalent of any ion. This quantity, in round numbers 96,500 coulombs, is known as a **faraday**. If a quantity of one coulomb flows through a conductor each second, the rate of flow is called an **ampere**.

Whether water flows through a pipe — and the rate — depends not alone on the capacity of the pipe and the availability of water, but upon the difference of level of the ends of the pipe, so a current is assumed to flow when there is a difference of **potential** or **electromotive force** at the ends of the conductor under consideration. This difference of potential is measured in **volts**. The rate of flow of water in a pipe is also varied by the resistance offered by friction. Similarly, we regard the rate of flow of electricity as determined by the resistance of the conductor, and as a unit of measure we adopt arbitrarily, for reasons which do not concern us here, a column of mercury 106.3 cm. in length and of a uniform cross section of 1 sq. mm. and at  $0^{\circ}\text{C}$ . This quantity is called an **ohm**. The volt is, then, the intensity of electrical energy required to cause the flow of one coulomb per second across a conductor of a resistance of one ohm. These relations may be concisely expressed in terms of **Ohm's law**,  $C = E/R$ , where  $C$  = the quantity,  $E$  = voltage, and  $R$  = resistance. The total energy involved is, of course,  $C \times E$  and is measured in joules, and if we have a joule per second the quantity is known as a watt ( $= \frac{1}{746}$  of one horse power).

These units derive their names from noted investigators whose contributions to the subject are satisfactorily summarized in the *Encyclopedia Britannica*.

**Explanations of Electrolysis.** — From the earliest observation of the difference between conduction of the current by metals and by electrolytes, various views of the mechanism of the process have been advanced as, for example, that of Grotthus (1805) and that of Clausius (1857). (See text-books on Electro Chemistry.) There have been devised several general hypotheses concerning the relations between chemical and electrical energy, among which may be mentioned those of Davy (1806) and Berzelius (1812). The latter view held the attention and guided, largely, the course of chemical thought for many years. According to Berzelius, "Every chemical action is fundamentally an electrical phenomenon," and "Electricity is the first cause of all chemical activity." (For details consult histories of chemistry.)

Since the first test of a satisfactory hypothesis is that it must be in accord with the known facts, all these hypotheses, after having served their purpose, have been given up and at present the orthodox view of the situation is that evolved from the hypothesis of Arrhenius (1887). This hypothesis, while not wholly free from adverse criticism, has so served chemistry as a mode of classification and as a stimulus to discovery that it is perhaps properly regarded as one of three fundamental hypotheses, ranking with the atomic and kinetic-molecular hypotheses.

In 1887, Arrhenius (*Zeit. für Phys. Chem.*, Vol. 1, p. 631) called attention to the fact that van't Hoff's hypothesis (see p. 161), assumed by him to apply to the greater number of solutions, can be extended to cover electrolytes if we assume the "abnormally" high osmotic pressures, freezing points, etc., to be due to dissociation in solution, the dissociation being analogous to that of gaseous chlorine, bromine, iodine, etc., when heated. If, then, in any way a measure of the degree of dissociation can be determined, we can calculate the osmotic pressure of an electrolyte according to van't Hoff's rule.

In a previous article in 1884, Arrhenius had extended the hypothesis of Clausius, that electrolytes conduct the electric current by reason of minimal dissociation into electrically charged particles, and assumed that not only was electrolysis due to the presence of products of dissociation, but that this dissociation is very extensive in the case of good conductors and that in very dilute solutions the dissociation is practically complete. In 1887 (*Zeit. für Phys. Chem.*, Vol. I, p. 637) he says: "Each electrolyte, in aqueous solution, consists of partly active, partly inactive, molecules, and the latter by dilution convert themselves in active molecules (by dissociation), so that in an infinite dilution only active molecules exist." These active molecules he proposes to call ions, and assumes these ions to be "laden with heavy electrical charges of opposite types and hence can only be wholly separated from each other by the expenditure of energy and in this respect differ from the products of gaseous dissociation."

The hypothesis may be now restated in somewhat simpler terms and extended to cover certain modifications made necessary by subsequently discovered facts.

Substances which are conductors of the second class when in solution in water (and in a few other solvents) are assumed to be dissociated, partially at ordinary dilutions, into positively and



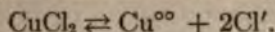
negatively charged portions called ions. The sum total of positive and negative electrical charges are equal.

**Ionization and Electrolysis.**—The process of electrolysis, in terms of the ionization hypothesis, may be supposed to proceed as follows:

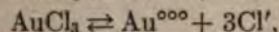
The poles of a source of electricity are kept at a constant difference of potential, *i.e.*, "voltage." If the poles are connected by means of a conductor, the current "flows," but the difference of potential is maintained by the generation of more electricity. If, now, these poles are connected by means of an electrolyte, ions positively charged (cations)\* are attracted to the negative pole and at the same time negatively charged ions (anions) are attracted to the positive pole. As each ion comes in contact with the electrode it is relieved of its charge and hence reverts to the behavior of the ordinary substance of the same composition. Thus if the electrolyte be common salt we have liberated at the electrodes sodium and chlorine. The sodium decomposes water thus:  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$  and hydrogen is evolved as a gas. What happens at the positive electrode, the anode, depends upon the concentration, temperature, etc. But in part, at least, chlorine is liberated as a gas. As soon as the equilibrium of the reaction between the dissociated and undissociated molecules, as indicated by the equation  $\text{NaCl} \rightleftharpoons \text{Na}^\circ + \text{Cl}'$ , is disturbed by removal of the ions the reaction goes on in the direction indicated by the arrow  $\rightarrow$  until practically all the salt is decomposed. It will be seen, then, that the charged ions are present in the solution **before connection is made with the battery**. Similar explanation in terms of the hypothesis may be offered for the progress of the electrolysis of any electrolyte.

**Amounts of Electricity Upon the Ions.**—In the electrolysis of hydrochloric acid 96,500 coulombs of electricity are required to liberate, simultaneously, a gram atomic weight of hydrogen and one of chlorine. It follows, therefore, that, while we may not know the actual number of ions, the ions of hydrogen and of chlorine bear equal, but opposite charges. It is conventional to represent these quantities, if positive, by the sign  $+$  or  $^\circ$  and, if negative, by the sign  $-$  or  $'$ . Thus  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}'$ , or  $\text{NaCl} \rightarrow \text{Na}^\circ + \text{Cl}'$ . The later convention represents the better usage. Again, if we electrolyze copper chloride,  $\text{CuCl}_2$ , we find (see p. 167) that

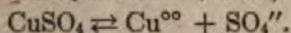
two chlorine ions are liberated for each one of copper and the condition of the salt in equilibrium in water may be indicated:



Again, similarly,



and



We may then say that the number of unit charges on an ion corresponds to the valence of the element or radical of which the ion is composed.

**Equilibrium in Electrolytes.**— If ionization is produced by the act of solution and the ions act as independent molecules carrying electrical charges, it is a necessary consequence that ionization be regarded as a chemical change and hence should conform to the general laws of equilibrium, and the condition of any ionized solute is that of a reversible reaction. If, for example, sodium chloride is in solution we would have  $\text{NaCl} \rightleftharpoons \text{Na}^{\circ} + \text{Cl}'$ . This situation is analogous with that of iodine vapor,  $\text{I}_2 \rightleftharpoons \text{I} + \text{I}$ .

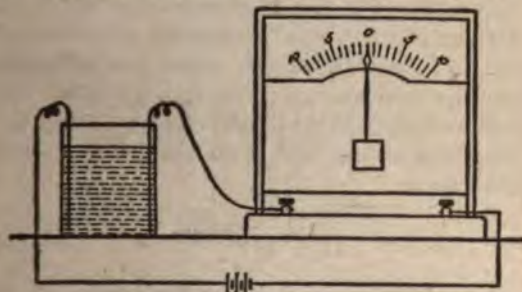


FIG. 52.

If water is the determining factor, dilution should drive the reaction to the right and removal of water to the left. That such is the general effect is shown by evaporation to dryness; when the result is non-conducting dry salt. If, on the other hand, we place a saturated solution of salt between the electrodes in a trough connected with an ammeter, as in Fig. 52, in such manner that on the addition of water, itself a non-conductor, the whole solution remains between the electrodes, the solution increases in conductivity. Since the ease with which a solution conducts a current is supposed to depend upon the capacity of the ions, their speed and their number, and since in this case, if we keep the temperature



constant, neither capacity nor speed can reasonably be assumed to change, the increased rate of transference can only be occasioned by increase in the number of ions. This is also to be expected from the law of chemical equilibrium. If we represent by  $C_1$  the concentration of sodium chloride in gram molecules per liter, and by  $C_2$  and  $C_3$  the concentration of the ions, then  $C_2 \times C_3 / C_1 = K$  (cf. p. 135). If we recall that  $C_1$  is the original amount of salt placed in solution, less that ionized, we may write the expression  $x^2 / (1 - x) = K$ , where  $x$  represents the concentration of each ion. If now we dilute the solution, say tenfold,

$$\frac{\left(\frac{x}{10}\right)^2}{\frac{1-x}{10}} = K, \text{ or } \frac{x^2}{(1-x)10} = K, \text{ or in general, } \frac{x^2}{(1-x)v} = K.$$

This, being interpreted, means that as  $v$ , the dilution of a solution, increases, the value of  $x$  must increase if the ratio is to remain constant. This relation, known as Ostwald's dilution law, holds, as rigidly as is to be expected, for all poor conductors. When applied to highly ionized substances good results are not obtained for reasons not yet satisfactorily explained, but which are perhaps to be found through a careful investigation of the hydration of the ions (*q.v.*). If in the consideration of ionic equilibrium we have to deal with a substance furnishing more than two ions, for example  $\text{CuCl}_2 \rightleftharpoons \text{Cu}^{++} + 2\text{Cl}'$ , we have

$$\frac{x^3}{(1-x)v} = K.$$

**Degree of Ionization.**—If water be added at successive intervals to a solution of sodium chloride in such manner as will keep all of the solution between parallel electrodes (see Fig. 52), at a fixed temperature, the conductivity will be found to increase with each addition of water until a maximum conductivity is reached. Subsequent additions of water do not materially affect the conductivity. This change of conductivity with dilution is illustrated by the graph given in Fig. 53. If the temperature is constant it may be assumed, without great error, that the amount of current which passes depends upon the number of ions present. When the conductivity reaches its maximum we may assume practically complete ionization. We call this value  $\lambda_\infty$ . At any lesser dilution, the conductivity, which we call  $\lambda_v$ , is less because fewer ions

are present. Therefore, the ratio  $\lambda_v/\lambda_\infty$  represents the degree of ionization of the salt. In the case of common salt  $\lambda_\infty$  is 110 at 18°, *i.e.*, its conductivity is 110 reciprocal ohms, sometimes called mhos. A normal solution of salt has a conductivity of 74.4 (*i.e.*,  $\lambda_v$  when  $v$  is 1000 cc. = 74.4 mhos). The degree of ionization of salt in normal solution is therefore  $74.4/110 = 0.676$  or 67.6 per cent. In a similar way the degree of ionization of other compounds has been determined.

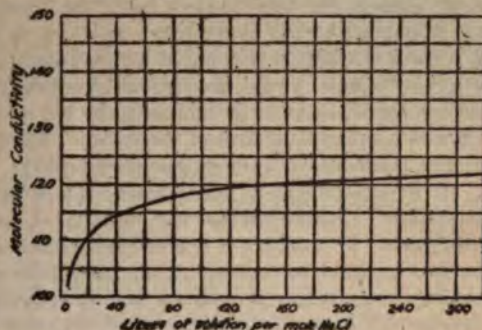


FIG. 53.

The following list gives the percentage ionization of some common compounds as determined by this method, at 18°.

	Per cent.		Per cent.
HCl 35 per cent.....	13.6	H <sub>2</sub> O.....	0.00001
HCl N.....	78.4	KOH N.....	77
HCl N/10.....	92.5	KOH N/10.....	91
HNO <sub>3</sub> 62 per cent.....	9.6	KOH N/100.....	97
HNO <sub>3</sub> N.....	78.9	NaOH N.....	72
HNO <sub>3</sub> N/10.....	92.1	NaOH N/10.....	91
HBr N.....	79	NaOH N/100.....	96
HBr N/10.....	93	Ba(OH) <sub>2</sub> N/100.....	93
HI N/10.....	91	NH <sub>4</sub> OH N.....	0.4
HClO <sub>3</sub> N.....	80	NH <sub>4</sub> OH N/100.....	1.3
HClO <sub>3</sub> N/10.....	93	NH <sub>4</sub> OH N/10.....	4.07
HMnO <sub>4</sub> N/2.....	93	NaCl N.....	74.1
H <sub>2</sub> SO <sub>4</sub> 95 per cent.....	0.8	NaCl N/10.....	85.2
H <sub>2</sub> SO <sub>4</sub> N.....	52	NaNO <sub>3</sub> N/10.....	83.2
H <sub>2</sub> SO <sub>4</sub> N/10.....	60.8	KCl N/10.....	86
H <sub>3</sub> PO <sub>4</sub> N/10.....	27	KBr N/10.....	85.9
H <sub>3</sub> AsO <sub>4</sub> N/8.....	19	KI N/10.....	86.9
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> N/10.....	30	NH <sub>4</sub> Cl N/10.....	85.2
H <sub>2</sub> F <sub>2</sub> N.....	7.9	K <sub>2</sub> SO <sub>4</sub> N/10.....	72.4
H <sub>2</sub> F <sub>2</sub> N/10.....	13	Na <sub>2</sub> SO <sub>4</sub> N/10.....	70.4
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> N.....	0.4	Ba(NO <sub>3</sub> ) <sub>2</sub> N/10.....	67.9
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> N/100.....	1.3	ZnSO <sub>4</sub> N/10.....	40.5
H <sub>2</sub> CO <sub>3</sub> N/100.....	0.24	CuSO <sub>4</sub> N/10.....	39.6
H <sub>2</sub> BO <sub>3</sub> N/50.....	0.003	HgCl <sub>2</sub> N/10.....	1
HCN N/16.....	0.01		



In actual practice the above method of obtaining the value  $\lambda_v$  is not used for many reasons, the most obvious being the impracticability of using cells of the size demanded by the description. It is convenient to determine the resistance of a cubic centimeter of solution in ohms and then express the conductivity in reciprocal ohms. To get the equivalent conductivity, the conductivity of 1 cc., the specific conductivity is multiplied by the number of cubic centimeters which contains a gram equivalent of the solute. For details of the methods used the student is referred to texts on electro-chemistry.

It is perhaps well at this point to call attention to the fact that it is also impossible to determine the conductivity at infinite dilution directly for all substances. Fortunately it is possible by determination of the relative speed of the ions to calculate the conductivity at infinite dilution. For those substances which become completely ionized only at such great dilutions that the errors of experiment vitiate the result the calculated value of  $\lambda_\infty$  is used.

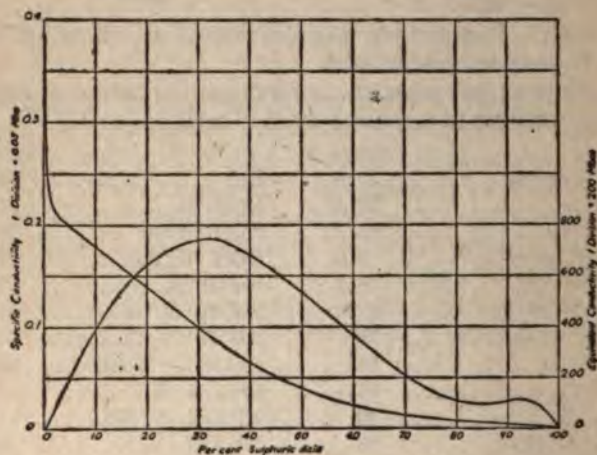


FIG. 54.

A third consideration may be mentioned. The degree of ionization is not to be confused with concentration of ions, nor the total conductivity of a solution containing a gram equivalent with the actual conductivity of a portion of the same. This may be illustrated by the curve, Fig. 54, which shows the change of specific conductivity with dilution and also the total or equivalent conductivity for sulfuric acid.

**Other Methods for Degrees of Ionization.**—The so-called abnormal depression of the freezing point, elevation of boiling point and osmotic pressure, if produced by reason of the dissociation of electrolytes, should also furnish means of calculating

the degree of dissociation. In most cases, though not in all, the results obtained accord as well as may be expected with those obtained electrolytically. The following table indicates the relative values obtained by three methods (modified from Nernst's Theoretical Chemistry). The same concentration of solutions is indicated for all three cases.

	Molar concentration.	Osmotic pressure.	Freezing point.	Conductivity.
Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$ .....	0.18	74	73.5	73
Magnesium sulfate, $\text{MgSO}_4$ .....	0.38	25	20.0	35.0
Strontium chloride, $\text{SrCl}_2$ .....	0.18	84.5	76.0	75.5
Potassium chloride, $\text{KCl}$ .....	0.14	81.0	86.0	86.0
Lithium chloride, $\text{LiCl}$ .....	0.13	92.0	94.0	84.0
Magnesium chloride, $\text{MgCl}_2$ .....	0.19	85.5	84.0	74.0

If the change of viscosity with change of concentration of solution be taken into account in the determination of  $\lambda_p/\lambda_\infty$ , it has been shown by A. A. Noyes that the degree of dissociation of most salts as determined by the freezing point and conductivity methods agree with each other within 2 per cent up to a concentration of 0.1 normal. The change of degree of dissociation with change of temperature is also shown to be slight and between  $0^\circ$  and  $18^\circ$  is less than the probable error of experiment (see Noyes & Falk, Jour. Am. Chem. Soc., Vol. 34, p. 487, 1912).

**Acids and Bases.** — So far we have purposely avoided defining these frequently used words, acid and base. We now have satisfactory terms in which to express these definitions. The term acid (from *acidus* = vinegar) was used by the alchemists to describe substances which had properties in common with vinegar and in contrast with the term **alkali** (from the Arabic for ashes) used for substances resembling the extract of ashes. Acids are sour, change the color of many vegetable colors, dissolve many solid substances which are insoluble in water, and lose these properties when brought in contact with alkalies. Alkalies are bitter, have "soapy" properties, are solvents for oils, and restore the color of dyes which have been changed by acids. In general the substances are of opposing characteristics. The products of their interaction are similar in many respects to common salt (*sal murias*) and hence are called salts. Gradually it was recognized that many



substances, not soluble in water, not affecting plant colors, etc., could, however, affect acids. Such substances were the oxides of known metals and a group of substances known as "earths," of which alumina ( $\text{Al}_2\text{O}_3$ ) is an example. In 1744, Rouelle employed the term base to include alkalies, earths, and oxides of metals. As accurate knowledge of chemical facts increased it became increasingly difficult to classify substances under the three heads, acid, base and salt. For example, the products of reaction of certain bases with acids may still be sour or may color litmus red or

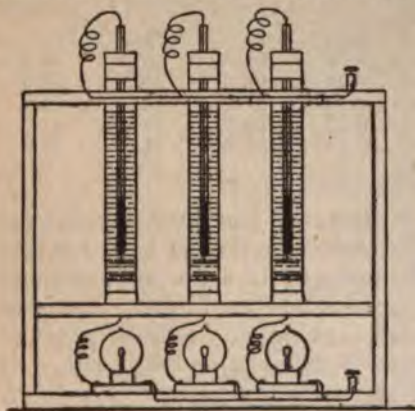


FIG. 55.

blue. It is also true that many substances not sour and not affecting litmus may otherwise behave as acids. We have seen that Lavoisier regarded the presence of oxygen as essential to acids and looked upon the oxides of the non-metals as the true acids. Davy (1810 *et seq.*) showed this view to be incorrect in respect to the halogen acids and that hydrogen is essential to the possession of acid properties. This view was fully confirmed by Graham (1833) and ex-

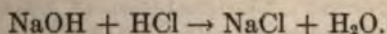
tended to all acids through his researches on the phosphoric and arsenic acids. (See *Alembic Club Reprints*, No. 7.) Further, it became clear that oxides dissolved in water may not only produce acids, but also bases. If, then, we wish precise terms, we must either yield these or secure sharper definition of them. The terms are so firmly grafted upon our language that their elimination is impossible even were it desirable. Exact definitions are not, of course, always essential, but clear ideas of relationship are, and the ionization hypothesis furnishes an especially satisfactory view of the relationship between acids and bases.

If we take equivalent, *e.g.*, normal, solutions of hydrochloric, sulfuric, and acetic acid and place equal quantities in contact with pieces of zinc of equal size, hydrogen will be liberated from all three acids (*cf.* p. 57). This is a typical acidic property and if we keep the temperature constant the relative rate of evolution

of hydrogen may be considered a measure of the relative activity, or strength, of the acids. If now we electrolyze solutions of these acids we find that hydrogen is liberated at the cathode and close examination reveals the fact that hydrogen is the only constituent they possess in common. If we examine their relative conductivities by means of the apparatus suggested by Whitney (Fig. 55) we find these in the same order as their activity upon zinc. The degree of dissociation,  $\lambda_v/\lambda_\infty$ , is also in this same order. Taking into account such facts as these we may consider that an acid is any substance which in aqueous solution, without hydrolysis, furnishes hydrogen ions, as the sole positive ion. Strong acids are those showing a high degree of ionization. Weak acids ionize but slightly. Acidity is then due to hydrogen ions and the activity of acids is a measure of the concentration of hydrogen ions.

In a similar manner we may compare the activities, common factor and conductivity of bases, and reach the conclusion that a base is any substance which in aqueous solution, without hydrolysis, furnishes hydroxyl ions. The concentration of hydroxyl ions determines the activity of a base. The oxides which react with acids to produce salts may therefore be regarded as basic while those which react with bases are acidic.

**Neutralization.**—When a solution of a strong acid (*e.g.*, HCl) is added dropwise to a solution of a strong base, *e.g.*, NaOH, gradually the base loses its characteristic effect on litmus and likewise the acid. If, now, the solution be evaporated to dryness, a residue of salt is formed. We may express this:



Obviously, however, the situation is more complex, since we have  $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}'$  and  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}'$ . (See table, page 175.) Water is a non-conductor and but slightly ionized, hence  $\text{H}^+ + \text{OH}' \rightarrow \text{H}_2\text{O}$  and consequently both acid and base lose their characteristic behavior, since only negligible quantities of hydrogen and hydroxide ions remain. On the other hand,  $\text{Na}^+ + \text{Cl}' \rightleftharpoons \text{NaCl}$  only to a moderate degree when in solution and complete conversion to salt is only effected by complete removal of water. This picture of the process of neutralization is to a very great extent confirmed by the fact that very dilute solutions of different acids, hence completely ionized, give the same heat of neutralization, *viz.*: 13,700 cal. per gram equivalent, since water alone



is formed; whereas concentrated acids with concentrated bases give varying heats of neutralization, as should be the case if, in addition to water, salts of different heats of formation, are produced. Confirmation is also brought forward by the fact that dilute solutions of salts may be mixed with no change of temperature, as was shown to be the case in 1841 by Hess (Law of Thermo-neutrality).

**Indicators.** — There are certain compounds which have one color in acid solution and a different color in alkaline solution. These are known as indicators. The greater number of them are organic compounds, though certain inorganic substances vary in color under the conditions cited. The indicators most commonly employed at present are litmus — red in acid, blue in basic solutions; phenolphthalein — colorless in acid, red in basic solutions; methyl orange — rose red in acid, yellow in basic solutions; Congo red — red in basic, blue in acid solutions.

A neutral solution is one in which the concentration of hydroxyl and of hydrogen ions is equal. Since the ionization of water is but one part in ten million a very slight increase in the concentration of either ion very nearly completely suppresses the ionization of the other. If then an indicator, very sensitive to the presence of an excess of hydroxyl ions, is added to a solution of an acid and a base is slowly added, as soon as all hydrogen ions are converted to water a very slight excess of hydroxyl ions will change the color of the indicator. The operation may be reversed by adding acid to a base, using an indicator very sensitive to an excess of hydrogen ions. The operation of thus ascertaining the concentration of an unknown solution by using one of known concentration together with an indicator is known as **titration**. The method is frequently employed for quantitative analysis and may be used for other substances than acids and bases.

The substances listed above are by no means the only indicators and literally hundreds of plant extracts, such as an infusion of red cabbage, of violets, etc., are subject to such color changes. Litmus is nearly equally sensitive to both hydrogen and hydroxyl ions. It is estimated that a concentration of  $0.0_{\text{s}}1$  gram molecules per liter of hydrogen ions or of from  $0.0_{\text{s}}1$  to  $0.0_61$  gram molecules per liter of hydroxyl ions will affect its color. The corresponding concentrations are for phenolphthalein  $0.0_71$  for hydrogen ions and  $0.0_41$  for bases; for methyl orange  $0.0_21$  for acids and  $0.0_{\text{s}}1$  for

bases. For a discussion of the theory of indicators see Stieglitz, *Am. Chem. Jour.*, vol., 39 (1908).

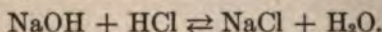
**Salts.**—When a base is neutralized by an acid we have water formed and a more or less extensive union of the remaining ions according to the dilution of the solution. This union of course becomes complete upon removal of the water. In the case above cited,  $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$ , we have common salt. Similar products resulting from other acids and bases are known as salts. We may therefore say that **a salt is the product, other than water, when a base reacts with an acid.** This view of the nature of a salt is particularly happy, since we group a large variety of substances under this head. When equivalent concentrations of acids and bases react with each other the salt produced is called a neutral salt without regard to the behavior of the salt toward indicators when in solution (*cf.* hydrolysis, p. 182). We may have other sorts of salts. For example, we may add to a fixed quantity of sulfuric acid sufficient sodium hydroxide to just half neutralize it. If we now remove the water by evaporation we have a salt,  $\text{H}_2\text{SO}_4 + \text{NaOH} \rightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$ . Salts of this type which still contain a part of the acid hydrogen are called **acid salts**. Other examples are furnished by the salts  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . Similarly, we may have **basic salts** which still retain a portion of the unneutralized hydroxyl of the base. Examples are furnished by the basic salts of lead, bismuth, copper, etc. (*q.v.*). Obviously, from the above considerations, it should be possible for salts to be formed by partial neutralization of a polybasic acid by each of two bases, or of a polyacid base by two acids and so obtain **mixed salts**. Examples are sodium potassium sulfate ( $\text{NaKSO}_4$ ); Rochelle salts ( $\text{NaKC}_4\text{H}_4\text{O}_6$ ); bleaching powder ( $\text{CaClOCl}$ ), etc. Also since one salt may unite with another, as will be shown later, (*vide* molecular compounds), we have also a class of salts known as **double salts**. Examples are potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ , alum,  $\text{KAl}(\text{SO}_4)_2$ , etc.

**Other Methods of Salt Formation.**—Though salts may be regarded as produced by reaction between a base and an acid, there are many methods by means of which the same compounds may be obtained. The following list gives the more important of these together with an equation illustrative of each method.

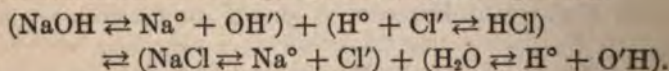


1. Neutralization of acid by a base:  $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ .
2. An acid and a metal:  $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$ .
3. An acid and an oxide:  $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$ .
4. A salt with an acid:  $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$ .
5. A salt with a base:  $\text{K}_2\text{SO}_4 + \text{Ba}(\text{OH})_2 \rightarrow \text{BaSO}_4 + 2\text{KOH}$ .
6. A salt with a salt:  $\text{KCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{KNO}_3$ .
7. By direct union of the elements:  $\text{Au} + 3\text{Cl} \rightarrow \text{AuCl}_3$ .
8. By displacement of one metal by another:  $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$ .

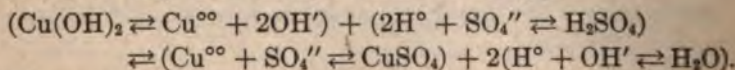
**Hydrolysis.** — It will be recalled that one of the important chemical properties of water is called hydrolysis and its discussion was deferred. (See p. 81.) We are now in a position to discuss the subject. When **neutral** salts are dissolved in water and tested with litmus we find no reaction in some cases, *e.g.*, common salt and potassium chloride; in other cases the reaction is acid, *e.g.*, copper sulfate and ferric chloride; in still other cases the reaction is basic, *e.g.*, sodium carbonate and sodium borate. In terms of the ionization hypothesis this behavior of salts is to be expected from a consideration of neutralization as a reversible reaction, thus



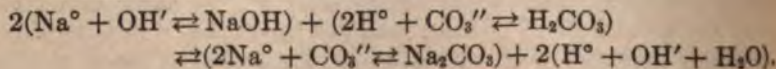
It is assumed that while the ionization of water is slight (see page 175), yet there are hydroxyl and hydrogen ions present and the complete statement of the equilibrium may be expressed:



Since, however, sodium hydroxide and hydrochloric acid are nearly equally ionized (*cf.* p. 175), there is no great excess of either hydroxyl ions or of hydrogen ions. The reaction is then neutral. However, we may have an equilibrium of the type:



In this equilibrium we have a weak base and a strong acid and hence an excess of hydrogen ions, hence the acid reaction. In a third case we may have



Here we have a strong base with a weak acid and hence an excess of hydroxyl ions with consequent basic reaction.

A fourth case may be distinguished. Suppose it were possible to make a solution of a salt of a weak base with a weak acid. We should expect that in such case hydrolysis would effect complete dissociation since both hydroxyl and hydrogen ions would be withdrawn to form the undissociated base and acid. Consequently, when the attempt is made to form such salts in solution or to dissolve them in water hydrolysis effects practically complete decomposition. Examples of such salts are aluminium carbonate, ferric acetate, etc. Complete dissociation of such salts is further favored if one or both of the products of hydrolysis are insoluble.

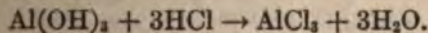
We may then classify the behavior of neutral salts with water as follows:

1. Strong acids with strong bases give salts neutral in solution.
2. Strong acids with weak bases give salts acid in solution.
3. Weak acids with strong bases give salts basic in solution.
4. Weak acids with weak bases give salts completely decomposed by water.

Since acids and bases of all degrees of dissociation exist it will be obvious that though we may distinguish the above classes of salts yet examples will occur where any degree of hydrolysis may be found. Only where equally strong acids and bases form a salt will exact neutrality be found. In such cases as sodium chloride or sodium sulfate the variation from neutrality is not sufficient to be indicated by litmus. The situation may be shown as a continuous series by the following diagram:

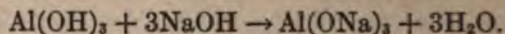
strong acids slight hydrolysis	moderate hydrolysis	weak acids great hydrolysis
strong bases		weak bases

**Amphoteric Substances.**—A very interesting example of continuity is furnished by the difficulty of determining whether a given substance is an acid or base. An illustration will be helpful: If aluminium hydroxide is treated with an acid it dissolves to form a salt:

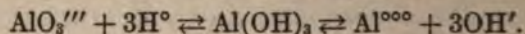




This behavior of the hydroxide is basic. It also dissolves in bases to form salts:



This behavior is acidic. In terms of the ionization hypothesis we must have with  $\text{Al}(\text{OH})_3$  the following equilibrium in solution:



It is then at one and the same time acidic and basic. This sort of behavior is not unusual and substances showing both acidic and basic behavior are called **amphoteric** (*αμφότεροι* = both of two). We may then regard compounds which are capable of furnishing both hydrogen and hydroxyl ions as forming a series as illustrated by the diagram:

acids	amphoteric substances	bases
furnishing $\text{H}^\circ$ only	furnishing both $\text{H}^\circ$ and $\text{OH}'$ at the same time	furnishing $\text{OH}'$ only

**Chemical Activity of Aqueous Solutions.** — Attention has already been directed to the "catalytic" effect of water in hastening the rate of certain reactions (p. 57 and p. 81). It is also true that in many cases the character of the change which takes place is affected by the presence of water. For example: If ammonium carbonate and copper nitrate are heated together while dry a very complex reaction takes place. The products of the reaction are cuprous oxide, cupric oxide, carbon dioxide, nitrous oxide, nitric oxide, nitrogen, and ammonia. On the other hand, if solutions of the two salts are mixed immediate reaction takes place, without heating. The reaction may be expressed by  $\text{Cu}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_4\text{NO}_3 + \text{CuCO}_3$ . The copper carbonate is precipitated.

Many other cases might be cited in which a similar catalytic and directive effect of water is evident. In practically all cases investigation shows that we are dealing with electrolytes. In terms of the ionization hypothesis the explanation is simple. If solutions of electrolytes already contain free charged ions and such solutions are mixed then reaction between ions of opposite type occurs at a rate and to an extent which depends upon the original concentration of the ions present and the degree of ionization and the solubility of the resulting products. If now by

the formation of slightly ionized or insoluble substances the ions originally present are removed, the principle of chemical equilibrium should operate to cause continual ionization of the original substances in solution. Such reactions in solution should be rapid since only this readjustment of free moving particles is accomplished. The possibility that catalytic and directive effects of water, as shown by aqueous solution, may be due simply to the intimacy of contact thus secured is excluded for the following reasons: All aqueous solutions do not show rapidity of reaction in excess of that shown in the dry state. Also solvents other than water should act in like manner, and such is not the case. For example, iodine and yellow phosphorus in the dry state react vigorously. Solutions of these elements in carbon disulfide react only slowly. The argument might be extended and examples multiplied with the result as stated: **The catalytic effect of water in hastening the chemical reactions of electrolytes and the directive effect of water on the character of the reactions produced depend on the presence of the free ions of the electrolytes in solution.**

**Summary.** — We may now summarize the facts and hypotheses considered in this chapter.

From the fact that in general equimolecular concentrations of compounds have the same quantitative effects upon the osmotic pressure, boiling point, and freezing point of solutions (when these solutions are not electrolytes), we have the hypothesis advanced as an explanation: **Substances in solution behave as if they were in gaseous condition confined to the volume of the pure solvent (called van't Hoff's Theory of Solution).**

The apparent exceptions to this general statement furnished by electrolytes are brought into conformity with it through the assumption of Arrhenius, that in the latter cases **ionization takes place to a greater or less degree and the "abnormal" results are due to the increase in the number of component parts of the solute.** The advantages of this explanation are that it furnishes a means of correlation of not only the facts of osmotic pressure, freezing points and boiling points, but also of electrolysis and the catalytic and directive effects of water as a solvent.

The latter hypothesis also lends plausible explanation to the processes of neutralization and hydrolysis and furnishes us with artificial means of determination of the limits of classes of compounds not otherwise readily defined. The hypotheses also have stimulated



chemists to make numerous investigations which have led to the discovery of many valuable facts and, as will appear subsequently, promise to make possible mathematical expression of chemical facts to a degree not at present attainable by other means. It is perhaps unfortunate that in some respects the hypotheses are bizarre and are not in accord with known facts and that some problems which ought to be solved by use of them are still not capable of solution. There are not a few chemists who for reasons which seem sufficient to them refuse to accept the hypotheses and deny both their validity and utility and consequently a fair presentation of the subject could not be made without calling attention to some of these points.

**Objections to Arrhenius' Hypothesis.** — It is not the present purpose to present a full discussion of these objections nor to attempt to answer satisfactorily all those cited, but simply to indicate the character of them and the direction from which satisfactory answers may come:

1. When such a substance as common salt ionizes the ions can scarcely be considered as anything but sodium and chlorine, and even though the ions are carrying charges of electricity we might expect that the behavior of the substances would more closely resemble their ordinary modes of action; yet sodium ions and chlorine ions are very soluble and without any of the ordinary characteristics of the corresponding elements. Of course, we realize that 96,500 coulombs of electricity, if present on an equivalent weight in grams of an ion, may reasonably be sufficient to materially affect the behavior of the ion as compared with the same substance minus that charge, and also, as we shall see, if the electronic hypothesis (*q.v.*) is correct, the ions are different substances in fact from the atoms of which they are chiefly composed.

2. If the ions are sufficiently free and independent to act as individual molecules, in the sense demanded by the gas laws, and yet carry such relatively enormous static electrical charges, how can they remain free in view of the known tendency of electrical charges of opposite sign to attract and mutually destroy each other?

A partial answer to this is found in the presumption, not of a static condition of the ionization, but of a kinetic equilibrium, *i.e.*, the ions do continually meet and discharge each other, but what we measure is the ratio of discharged to charged ions under given conditions. It is also assumed that the solvent actually tends to insulate the ions in the same manner that the walls of a Leyden jar insulate the charges of static electricity and Nernst and Thompson attempt to relate the degree of ionizing capacity of a solvent with its insulating power, its dielectric constant, but it must be confessed that a wholly satisfactory answer to the objection is not at hand unless it be found in the hydration theory (*q.v.*).

3. If an ionized compound is a mixture of gaseous particles, why are they not separable into their components by diffusion processes? The answer to this objection is happily partly reached by experimental evidence that such is the

case; *e.g.*, in the preparation of one type of the concentration cell (*q.v.*), the most obvious explanation of which is through the assumption of such diffusion. That the separation of ions by diffusion is not readily accomplished is also to be expected because of the high electrostatic charges assumed to be present upon the ions.

4. If we consider that many acids, bases and salts which are highly ionized in solution are exothermic, it is to be expected that ionization would call for the absorption of energy and a very reasonable query is as to the source of supply of this energy. No wholly satisfactory answer is at hand, but it has been suggested that both the solute and the ions may unite with the solvent and the energy of this union is available for the separation. Indeed, very considerable evidence is at hand to show that such union actually does take place. (See Hydrate Theory.)

5. L. Kahlenberg (Jour. Phys. Chem., Vol. 5, p. 339) cites the most serious line of objections in which he shows that concordant results for measurement of the degree of ionization are not shown by the three methods of determining the same and that chemical activity of the catalytic and directive type cited on p. 184 are not shown by electrolytes alone. He also shows that increased conductivity is not always a function of the dilution, as is demanded by the hypothesis. In short, he is so unsatisfied with respect to the accord between fact and hypothesis that he rejects as relatively useless not only the hypothesis of Arrhenius, but also that of van't Hoff and subsequently (Jour. Phys. Chem., Vol. 7) the conception of osmotic pressure as anything other than a special measure of the chemical affinity between solute and solvent. The whole situation may now be summed up as follows:

The ionization and related hypotheses are by no means a satisfactory and complete picture of the relation between solute and solvent in the group of substances which we classify under the head of solutions. That it is an approximation toward a true picture few deny. It is to be hoped that from the combination of Werner's theory (*q.v.*), the Solvate theory (*q.v.*), and the theory of Electrons (*q.v.*), may be born a view wholly consistent with fact, more useful for correlative purposes and for prophecy than is the present view.

**Exercises.** — 1. If a 1 per cent sugar solution at  $0^{\circ}$  shows an osmotic pressure of 518.8 mm. of mercury, calculate the molecular weight of sugar. Also express the molar strength of the solution.

2. From the solubility of common salt calculate the osmotic pressure of a saturated solution at  $0^{\circ}$  C., assuming that no dissociation takes place. Also calculate the osmotic pressure, assuming 50 per cent dissociation.

3. If a molar solution of common salt is 67.6 per cent dissociated, calculate the osmotic pressure at  $18^{\circ}$  C.

4. If 0.23 g. of alcohol in 100 cc. shows an osmotic pressure of 1.12 atmospheres, what is its molecular weight?

5. If alcohol shows a "normal" effect on the freezing point



of water, what is the freezing point of the solution cited in Exercise 4?

6. If 0.2735 gram of hydrogen peroxide dissolved in 19.86 grams of water shows a lowering of the freezing point  $0.746^{\circ}\text{C}$ ., what is the indicated molecular weight? What might be the cause of the deviation from the exact molecular weight "obtained from analysis"?

7. If 2.423 grams of sulfur dissolved in 100 grams of naphthalene show a lowering of the freezing point of  $0.641^{\circ}$ , what is the molecular weight of the sulfur? What is the apparent molecular complexity of sulfur?

8. A solution of a non-electrolyte in water has a concentration of 3.15 grams in 100 cc. and a freezing point of  $-0.279^{\circ}\text{C}$ . What is the molecular weight?

9. Copper sulfate in molar concentration in water shows a freezing point depression of  $2.3^{\circ}\text{C}$ . What is its percentage ionization?

10. What should be the boiling point of a solution of 10 grams of sugar dissolved in 100 grams of water?

11. The boiling point of 54.65 grams of carbon disulfide is raised  $0.486^{\circ}$  by 1.448 grams of phosphorus. What is the molecular weight of the phosphorus and what is the atomic complexity of the molecule?

12. What is the boiling point of a normal salt solution, provided the ionization at the boiling point were the same as at  $18^{\circ}$ ?

13. 42.5 grams of lithium chloride ( $\text{LiCl}$ ) in 500 cc. of water has a boiling point of  $100.97^{\circ}$ . What is the degree of dissociation?

14. What number of coulombs of electricity will be required to decompose 5 grams of copper sulfate; how many to decompose 3 grams of water?

15. Explain in terms of Arrhenius' hypothesis the interaction of iron and copper sulfate; of silver nitrate and sodium chloride; of zinc and hydrochloric acid.

16. State clearly the relation between the ionization hypothesis and the facts of osmotic pressure, freezing point depression, boiling point elevation, electrolysis and catalytic effects of water.

17. Define the term "ion" in terms of hypothesis and in terms of fact.

18. Make a list of the properties, physical and chemical, of the following ions:  $\text{Cu}^{\circ}$ ,  $\text{H}^{\circ}$ ,  $\text{K}^{\circ}$ ,  $\text{I}'$ ,  $\text{Cl}'$ ,  $\text{OH}'$ .

19. Make a table of the salts mentioned in the text up to the

end of Chapter IX and classify them as neutral, acid, basic, mixed or double.

20. May neutral salts be acid in reaction when in solution? Why? Can an acid salt be alkaline in reaction when in water? Why?

21. If  $\lambda_{\infty}$  of copper sulfate is 156 and  $\lambda_{\nu}$  is 110, what is the degree of dissociation? What effect is produced by increasing and what by decreasing the concentration?

22. Calculate the value of the ionization constant for acetic acid for normal and N/10 concentrations.

23. State exactly what is meant by the terms strong acid, and strong base in (a) terms of the ionization hypothesis and (b) facts.

24. If the ionization hypothesis does not harmonize with known facts, why is it not rejected?

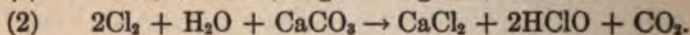
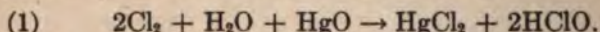
25. Define acid, base, salt, neutral salt, basic salt, mixed salt, using the terms (1) "the formula of which contains," (2) "which ionizes into," and (3) "is formed by."



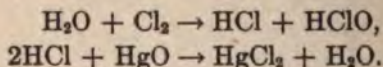
## CHAPTER X

### OXYGEN ACIDS OF THE HALOGENS

**Preparation of Hypochlorous Acid and Its Salts.**—As already mentioned (p. 121) chlorine when dissolved in water reacts as indicated by the equation,  $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{HCl}$ . This equilibrium is not self-evident, since the solution shows the characteristic color and odor of chlorine (*cf.* also p. 131). Small quantities of acid exist in the solution as indicated by the fact that litmus solution is reddened by it before being bleached. Also small quantities of hypochlorous acid may be obtained by distillation. In such an equilibrium system we should expect that treatment with a substance capable of reacting with the stronger acid, HCl, but not readily with the weaker would disturb the system in the direction of the arrow ( $\rightarrow$ ). This result is obtained when the system is treated with either mercuric oxide or with calcium carbonate in suspension in water. We may express the results by the equations:



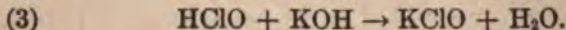
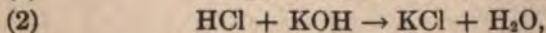
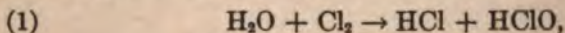
Equation (1) may be written in two steps:



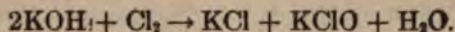
By addition of these two equations we get equation (1) above.

Hypochlorous acid may be separated from such mixtures in the form of a dilute aqueous solution by careful distillation. It is a very weak acid and is also unstable (*vide* p. 192).

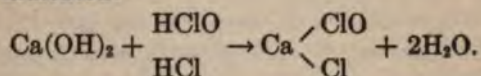
If we add chlorine to a dilute solution of a base both acids are neutralized as fast as formed. A mixture of salts is thus obtained. This may be indicated:



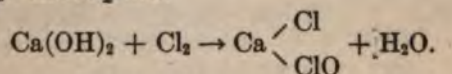
By addition we have,



Solutions of this type have powerful bleaching properties. The one indicated above was first prepared in 1785 by Berthollet. Later it was manufactured in large quantities at Javelle for bleaching purposes. It was therefore called Eau de Javelles. About 1820 it was found that sodium hydroxide could be used instead of potassium hydroxide and the bleaching solution was known as Labarraque's solution. At a still later date it was found that the still cheaper base, calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , could be employed. In this case it is possible that both acids may take part in the neutralization of a single molecule of the base, giving a mixed salt. This may be indicated:



This substance is readily prepared in the dry condition by passing chlorine through slaked lime:



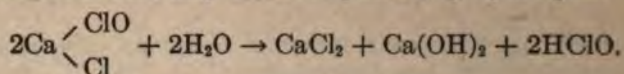
This substance is known as bleaching powder. (That the powder is really a mixed salt and not a mixture of calcium chloride,  $\text{CaCl}_2$ , and of calcium hypochlorite,  $\text{Ca}(\text{ClO})_2$ , is indicated by the fact that it is not deliquescent and is almost wholly insoluble in alcohol. Calcium chloride is both deliquescent and soluble in alcohol.)

It is probable that the reaction last indicated is not complete. If complete the substance when dry should contain about 49 per cent of "available chlorine" (see reactions 1 and 2 below). As a matter of fact only with the greatest care can the percentage of chlorine be raised to 43 per cent and the commercial bleaching powder ordinarily contains but 36 to 38 per cent. The powder is probably, therefore, a mixture of approximately  $2\text{CaClOCl}$  and  $\text{Ca}(\text{OH})_2$ , *i.e.*, two-thirds of the lime used is converted to the mixed salt. Such mixtures are sometimes expressed by formulæ, thus:  $2\text{CaOClCl} \cdot \text{Ca}(\text{OH})_2$ .

Bleaching powder is manufactured on an enormous scale and is used for purification of water, as a disinfectant and as a bleaching agent. The bleaching effect is due to the formation and subsequent

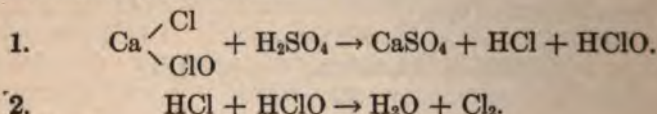


decomposition of hypochlorous acid (*vide infra*). The formation of hypochlorous acid may be accomplished by hydrolysis. Thus:

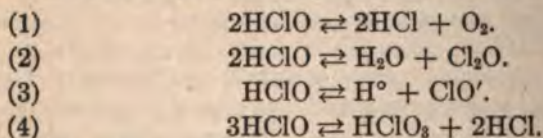


If acids are present the liberation of hypochlorous acid is more rapid and extensive than in water alone. The new process laundries use, instead of bleaching powder, a salt solution which has been electrolyzed. Electrolysis produces sodium hydroxide and chlorine, according to the equation  $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Cl}_2 + \text{H}_2$ . The chlorine and sodium hydroxide react to produce hypochlorite and chloride,  $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}$ . The electrolyzed solution is therefore Labarraque's solution. It is said to be cheaper than bleaching powder, which is used for the same purpose, and also to cause less damage to fabrics.

If bleaching powder is treated with strong acids chlorine is liberated. The reactions taking place are probably those indicated by the following equations:

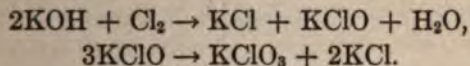


**Properties of Hypochlorous Acid.**—Hypochlorous acid is known only in dilute aqueous solution. It is a very weak acid and is also very unstable. It is capable of undergoing four different kinds of change according to conditions, thus:



It is probable that in a solution in water these four reactions are in equilibrium, or at least there is a tendency to establish equilibrium of these types. If now we modify the conditions the speed of the various reactions is not likely to be equally affected. If also the circumstances are such that a given product is removed as fast as formed the reaction which produces it will be facilitated. Light seems to hasten reaction (1) more than the others and since the solubility of oxygen is small, chlorine solutions when exposed

to the sunlight liberate oxygen. This is the reverse of Deacon's process (*q.v.*) (*cf.* also p. 116). Catalytic agents, such as silver oxide, copper oxide, etc., also favor this reaction. This removal of water would, of course, tend to favor the second reaction (2). The removal of either hydrogen ions or hypochlorite ions ( $\text{ClO}'$ ) causes continuance of the process of ionization, hence in the presence of bases the solution behaves wholly as an acid (*cf.* p. 134). Rise of temperature favors reaction (4) more than the others and consequently chlorine added to hot water produces some chloric acid,  $\text{HClO}_3$ . If reactions (1), (2), and (3) be inhibited by converting the acid to a salt, reaction (4) alone takes place when the solution is heated. Consequently hot solutions of potassium hydroxide, or of other bases, give solutions of salts of both chloric and hydrochloric acids when treated with chlorine. These changes may be represented in two stages by the following equations:

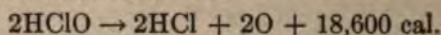


By addition we have  $6\text{KOH} + 3\text{Cl}_2 \rightarrow \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O}$ . Potassium chlorate,  $\text{KClO}_3$ , is the raw material used in the preparation of several of the other compounds of chlorine.

**Bleaching.**—As noted above (1), hypochlorous acid decomposes spontaneously into oxygen and hydrochloric acid. If readily oxidizable substances are present this reaction should continue so long as the oxygen is removed. Many colored substances are readily oxidized and the oxidized products are frequently either colorless or less highly colored. If, then, solutions of chlorine or of hypochlorites be brought into contact with such colored substances "bleaching" results (German *bleichen* = to whiten). It may be recalled that bleaching of clothing is an ancient household process carried out ordinarily by moistening the cloth and exposing it to the action of air and sunlight. The reaction is very slow. The process of bleaching by means of hypochlorous acid is very rapid. When we consider that in bleaching by chlorine we must first form and then decompose hypochlorous acid it may seem surprising that the process is more rapid than the action of free oxygen. Formerly the explanation offered was that oxygen just liberated from a compound, nascent, is atomic, not molecular, and is therefore more active. It seems more reasonable, however, that the proper explanation is as follows: hypochlorous acid



is an endothermic compound. Its decomposition is therefore attended by the evolution of heat:



We have already seen (p. 142) that reactions take place the more readily the greater the liberation of energy which accompanies them. For a process involving the consumption of a gram molecular weight of oxygen 18,600 calories of heat are produced with hypochlorous acid in excess of the quantity produced if free oxygen is employed. Hypochlorous acid should be therefore, as it is, a more vigorous oxidizing agent than oxygen.

**Nomenclature of Oxides, Oxygen Acids, and Salts of the Halogens.** — Below is given a table of the known compounds of the halogens containing oxygen, together with the names:

Chlorine.	Bromine.	Iodine.
$\text{Cl}_2\text{O}$ , chlorine monoxide	.....	$(\text{I}_2\text{O})$ , iodine monoxide
$(\text{Cl}_2\text{O}_3)$ , chlorine trioxide	$(\text{Br}_2\text{O}_3)$ , bromine trioxide	$(\text{I}_2\text{O}_3)$ , iodine trioxide
$\text{ClO}_2$ , chlorine dioxide	.....	.....
$(\text{Cl}_2\text{O}_5)$ , chlorine pentoxide	$(\text{Br}_2\text{O}_5)$ , bromine pentoxide	$\text{I}_2\text{O}_5$ , iodine pentoxide
$\text{Cl}_2\text{O}_7$ , chlorine heptoxide	$(\text{Br}_2\text{O}_7)$ , bromine heptoxide	$(\text{I}_2\text{O}_7)$ , iodine heptoxide
$\text{HClO}$ , hypochlorous acid	$\text{HBrO}$ , hypobromous acid	$\text{HIO}$ , hypoiodous acid
$\text{HClO}_2$ , chlorous acid	$(\text{HBrO}_2)$ , bromous acid	$(\text{HIO}_2)$ , iodosous acid
$\text{HClO}_3$ , chloric acid	$\text{HBrO}_3$ , bromic acid	$\text{HIO}_3$ , iodic acid
$\text{HClO}_4$ , perchloric acid	.....	$\text{HIO}_4$ , periodic acid
$\text{MClO}$ , -hypochlorite	$\text{MBrO}$ , -hypobromite	$\text{MIO}$ , -hypoiodite
$\text{MClO}_2$ , -chlorite	$(\text{MBrO}_2)$ , -bromite	$(\text{MIO}_2)$ , -iodite
$\text{MClO}_3$ , -chlorate	$\text{MBrO}_3$ , -bromate	$\text{MIO}_3$ , -iodate
$\text{MClO}_4$ , -perchlorate	.....	$\text{MIO}_4$ , -periodate

(Compounds indicated by parentheses are not yet isolated, but derivatives indicating their existence are known.)

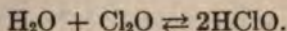
The oxides of the halogens are usually named by using numeral prefixes to indicate the amount of oxygen in the formula weight, thus chlorine monoxide ( $\text{Cl}_2\text{O}$ ), chlorine dioxide ( $\text{ClO}_2$ ), chlorine heptoxide ( $\text{Cl}_2\text{O}_7$ ). Some of the oxides bear the relation to the acids of being anhydrides and hence at times names indicating this relation are used, thus  $\text{I}_2\text{O}_5$  is iodic anhydride,  $\text{Cl}_2\text{O}$  hypochlorous anhydride, etc.

In naming the oxygen acids the ending, *ic*, usually appended to a root form derived from the name of the characteristic element, is used to designate the normal compound of the sort. This is usually the first discovered or at least the best known compound of the

group, thus chloric ( $\text{HClO}_3$ ), bromic ( $\text{HBrO}_3$ ), iodic ( $\text{HIO}_3$ ) acids. The acid containing one atomic weight less of oxygen per molecule is called by a name ending in *ous*, thus chlorous acid ( $\text{HClO}_2$ ), etc. If other acids are known prefixes are used. For the acid containing less oxygen than the *ous* acid the prefix *hypo* is used (from  $\text{ὑπο}$  = below). Thus, hypochlorous acid ( $\text{HClO}$ ), hypoiodous acid ( $\text{HIO}$ ), etc. Acids higher in oxygen content than the *ic* acid are distinguished by the prefix *per* (*per* = through or beyond). Thus, perchloric acid ( $\text{HClO}_4$ ) etc. It is especially advantageous that this simple system suffices to carry the nomenclature of all acids. Later we shall meet with modifications of some of these types but no change in the system here indicated is involved (see ortho, meta, and normal acids).

Salts are named by use of the name of the metal prefixed to the name of the acid modified to end in *ate* for *ic* acids and to *ite* for *ous* acids, thus sodium hypochlorite ( $\text{NaClO}$ ), sodium iodate ( $\text{NaIO}_3$ ), etc. This system is fortunately also uniform for all salts.

**Chlorine Monoxide.**—Chlorine monoxide is an endothermic compound and is not prepared by direct union of the elements. In addition to the dehydration of hypochlorous acid (not very practicable) it may be obtained by treatment of freshly prepared mercuric oxide with chlorine. The reacting materials must be kept cold in order to prevent decomposition of the chlorine monoxide. The reaction is indicated by  $2\text{HgO} + 2\text{Cl}_2 \rightarrow \text{Hg}_2\text{OCl}_2 + \text{Cl}_2\text{O}$ . The gas may be condensed to liquid form by passing it into a U tube immersed in an ice and salt mixture. The liquid is reddish brown and boils at about  $15^\circ \text{C}$ . It, therefore, evaporates rapidly at room temperature to an orange yellow gas. It is soluble in water (200 vol. to one of water), which solution acts as hypochlorous acid:



Both liquid and gas are explosive, the former particularly so, and react with explosive violence with many substances such as phosphorus, sulfur, turpentine, rubber, etc. Its molecular weight by vapor density is 86.92, corresponding to the formula given. It has no commercial applications.

**Chlorine Dioxide.**—This substance, known also as chlorine peroxide, was first prepared by Humphry Davy (1811). Its

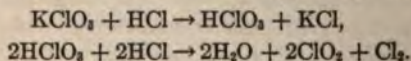


composition was first established by Gay-Lussac and shown to correspond to the formula  $\text{ClO}_2$ . It is most readily prepared by treatment of potassium chlorate with sulfuric acid. The reaction is represented by the equations,  $2\text{KClO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HClO}_3$ , and  $3\text{HClO}_3 \rightarrow \text{HClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O}$ . If the temperature at which the reactions take place is not kept at, or below, about  $15^\circ$  a violent explosion may take place, due to the spontaneous decomposition of the dioxide. The substance is a yellow gas, boiling point  $10^\circ$ . It is a very powerful oxidizing agent.

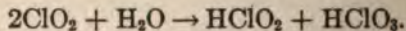
When powdered potassium chlorate is placed in a strong walled cylinder and covered with concentrated sulfuric acid the cylinder slowly fills with a brownish yellow gas. Immersion of a hot wire into the gas produces a violent explosion. The operator should protect himself from possible damage from flying glass or acid.

If a few grams of potassium chlorate are placed in a glass cylinder and covered with water and some small bits of yellow phosphorus are dropped into the water sulfuric acid may be introduced beneath the water by means of a pipette. The chlorine dioxide so produced causes the phosphorus to burn with great brilliancy. A mixture of powdered potassium chlorate and powdered sugar, powdered before mixing, may be ignited by means of a drop of concentrated sulfuric acid.

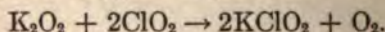
If potassium chlorate is treated with hydrochloric acid a mixture of chlorine and chlorine dioxide is obtained. This mixture was by Davy supposed to be a compound and was called *euchlorine*. It is a powerful oxidizing agent much employed in laboratory operations. The reactions may be expressed:



**Chlorous Acid and its Anhydride.** — When chlorine dioxide is dissolved in cold water and the solution is allowed to stand, a mixture of chlorous and chloric acid is produced. If this solution is neutralized a mixture of a chlorite and chlorate is obtained. The dioxide therefore reacts somewhat as would a mixture of chlorine trioxide,  $\text{Cl}_2\text{O}_3$ , and chlorine pentoxide,  $\text{Cl}_2\text{O}_5$  (cf. nitrogen peroxide, p. 294).



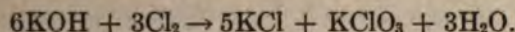
If potassium peroxide is added to a solution of chlorine dioxide potassium chlorite and oxygen are produced.



If this solution is acidified the solution probably contains free chlorous acid. Its anhydride should be chlorine trioxide, but

neither the free acid nor its anhydride have been prepared in pure condition.

**Potassium Chlorate and Chloric Acid.**—When chlorine is added to hot concentrated caustic potash a chlorate is produced (cf. p. 193). The reaction has been given:



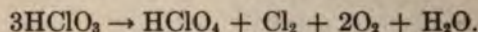
The products of this reaction may be separated by fractional crystallization. The first fractions which crystallize from a concentrated solution may be pure potassium chlorate. The solubility of the chlorate is 7.5 grams per 100 cc. of water at 20°. The solubility of the chloride is 34.5 grams under the same conditions. The solubility of both is about 56 grams at 100°. If then a solution of the two salts in the ratio formed in the above equation (i.e., approximately 3 parts of chloride to one of chlorate) were evaporated at 100° until on cooling to 20° it would be just saturated with chloride, there would be present in each 100 cc. approximately 11.5 grams of chlorate. Since its solubility is but 7.5 the remainder must separate out as a solid. A little consideration will make clear how this method may be used to separate to some extent any pair of salts of sufficient difference of solubility. The preparation of potassium chlorate is more cheaply effected by first preparing calcium chlorate:  $6\text{Ca(OH)}_2 + 6\text{Cl}_2 \rightarrow 5\text{CaCl}_2 + \text{Ca(ClO}_3)_2 + 6\text{H}_2\text{O}$ . A solution of the two salts is then treated with potassium chloride. The reaction which takes place may be indicated:  $2\text{KCl} + \text{Ca(ClO}_3)_2 \rightarrow 2\text{KClO}_3 + \text{CaCl}_2$ . The separation of these salts is the more readily effected since the solubility of the calcium chloride is 75 grams per 100 cc. at 20°. At present potassium chlorate is prepared almost exclusively by the electrolysis of hot solutions of potassium chloride. The change may be represented by one equation,  $\text{KCl} + 3\text{H}_2\text{O} \rightarrow \text{KClO}_3 + 3\text{H}_2$ , though unquestionably the electrolysis produces first chlorine, potassium hydroxide and hydrogen.

Potassium chlorate yields oxygen readily when heated (cf. p. 29). It forms mixtures with easily combustible substances which are highly explosive and subject to detonation by either shock or friction. Many severe accidents in laboratories and mills have been caused by such explosions. An illustration of this type of reaction may be shown by placing a few drops of a solution of phosphorus in carbon disulfide upon a very small quantity of



potassium chlorate. As soon as the disulfide has evaporated a violent detonation occurs.

Chloric acid is not readily prepared from potassium chlorate by the method commonly employed for the preparation of other acids, *viz.*, treatment of a salt of the acid sought with a less volatile acid. We have already seen (*cf.* p. 149) that if we attempt to use phosphoric acid the reaction would not only be slow but at the temperature required for distillation considerable decomposition of the chloric acid would occur. In this and similar cases we may use another method which also employs the principle of reversible reactions (*cf.* p. 132), *viz.*, to treat a solution of a salt of the acid sought with another which forms an insoluble compound with the metal ion of the salt. For example, we may treat a solution of barium chlorate with a dilute solution of sulfuric acid. The reaction is  $\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HClO}_3$ . The barium sulfate is almost absolutely insoluble in water. If equivalent quantities of the salt and acid are employed we have a pure solution of chloric acid. Solutions of chloric acid thus obtained may be concentrated in vacuo; at or below 40° (Fig. 30). When the acid has reached a concentration of 40 per cent decomposition begins and no greater concentration can be obtained. The reaction probably takes place as indicated:

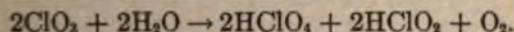


The concentrated liquid is viscid, colorless and ill smelling. It is a powerful oxidizing agent. If we attempt to prepare from it its anhydride,  $\text{Cl}_2\text{O}_5$ , the result is invariably the formation of chlorine dioxide and oxygen. The acid has no practical applications. Its salts, particularly potassium chlorate, are used extensively as oxidizing agents, in the manufacture of pyrotechnics chlorate powders, etc.

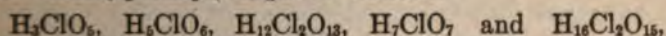
**Perchloric Acid.** — As has already been mentioned, when chloric acid is heated above 40° or allowed to stand in the light, perchloric acid is produced. It may also be obtained by distillation, under diminished pressure, of potassium perchlorate and sulfuric acid, though, as the writer knows to his sorrow, the reaction is a bit dangerous. It is obviously the most stable of the oxygen acids of chlorine. This fact harmonizes with the thermal relations of these acids as is shown by the following table:

	Heat of formation.	Heat per atom of oxygen.
HClO <sub>4</sub> .....	-700 cal.	-175
HClO <sub>3</sub> .....	-15,300 "	-5100
HClO.....	-9,300 "	-9300

The acid may be prepared by the electrolysis of chloric acid, and the salts by electrolysis of chlorates. The action is probably due to the anion ClO<sub>3</sub>, when discharged, reacting with water:



The pure acid can be prepared as a liquid with a specific gravity of 1.764, but is unstable in the light and when in contact with oxidizable substances, though less readily decomposed than chloric acid. It dissolves in water with the evolution of heat, forming a series of hydrates containing 1, 2, 2.5, 3 and 3.5 molecules of water. These, perhaps, might be written:



though probably no clearness is gained by so doing. The monohydrate HClO<sub>4</sub> · H<sub>2</sub>O has a definite melting point of 50° C. The relation between these hydrates and the hydrated acids later encountered is not rendered clearer by the fact that the constant boiling mixture at 203° C. and which contains 71.6 per cent acid does not correspond to any of the hydrates. Of this we shall have more to say later. The salts of perchloric acid are all soluble in water, but a pure salt of the acid may be quantitatively precipitated by adding perchloric acid to an alcoholic solution of potassium hydroxide, since it is wholly insoluble in alcohol. The salts are all derived from the monobasic acid HClO<sub>4</sub> (cf. periodic acid). They find application to some extent in pyrotechnics, being somewhat safer to handle than chlorates.

**Chlorine Heptoxide.** — If cold perchloric acid is treated with cold phosphoric anhydride and, after the reaction is over, the mixture is distilled at a temperature not above 82°, a colorless unstable oil is obtained. It has the composition represented by the formula Cl<sub>2</sub>O<sub>7</sub>. It is very unstable and reacts readily with water to form the acid.

**Structural Formulæ.** — When chlorine unites with hydrogen to form hydrochloric acid the relation is one to one in equivalents

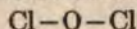


and the formula may be written to indicate the valence relation,  $\text{H}-\text{Cl}$ . The sign  $-$  simply indicates the valence of the two elements and may be regarded as being made up of two parts, one-half representing the valence of chlorine, the other that of hydrogen. Of course, since we have not the faintest idea of how the union of the two elements is mechanically effected, the sign  $(-)$  is simply a convention. Formulas which show the valence relations of the elements are variously called **graphic**, **constitutional**, or **structural** formulas. When oxygen is also in combination with chlorine and hydrogen the question of their valence relation rises. Is the relation to be represented in hypochlorous acid by the graph  $\text{H}-\text{O}-\text{Cl}$ ,  $\text{H}-\text{Cl}-\text{O}$ , or otherwise? It is perhaps impossible to give a positive answer to questions of this type. A study of the modes of formation of compounds and of their behavior frequently enables us to offer probable graphs which are useful in various ways. For example, the structural formula of chlorine monoxide is very probably  $\text{Cl}-\text{O}-\text{Cl}$  since oxygen is, as a rule, bivalent. We have abundant reasons for considering the valence relation in water to be  $\text{H}-\text{O}-\text{H}$ . Since hypochlorous acid is formed by reaction between water and chlorine monoxide the simplest formula would be shown

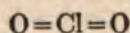
by the interchange  $\begin{array}{c} \text{Cl}-\text{O}-\text{Cl} \\ \diagup \quad \diagdown \\ \text{H}-\text{O}-\text{H} \end{array}$  giving  $2\text{H}-\text{O}-\text{Cl}$ .

The behavior of the acid accords with what we should expect from such a structure and we therefore believe it the most probable of the possible relations. In a similar manner a study of the formation and behavior of chlorine compounds has led to the following formulas:

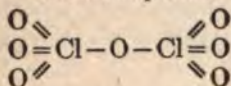
Chlorine monoxide



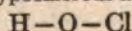
Chlorine dioxide



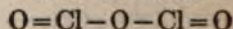
Chlorine heptoxide



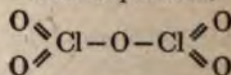
Hypochlorous acid



Chlorine trioxide



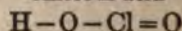
Chlorine pentoxide



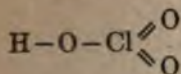
Hydrochloric acid



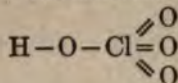
Chlorous acid



Chloric acid



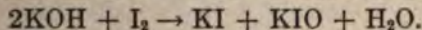
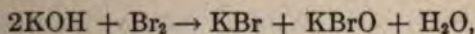
Perchloric acid



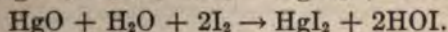
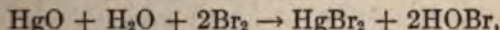
It is to be emphasized that the above formulas indicate only the probable order of combination of the constituent elements and that we have not attempted to give the reasons for the conclusions reached. If, however, the formulas are correct they indicate a valency for chlorine ranging all the way from one to seven.

***Hypobromous and Hypiodous Acids and Bromous Acid.*** —

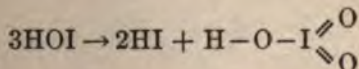
When bromine or iodine are added to cold solutions of bases colorless, or but slightly colored, liquids are obtained which have bleaching powers only less marked than those of hypochlorites. The reactions are doubtless:



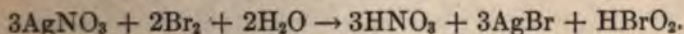
It is also probable that when bromine and iodine are dissolved in water small quantities of the corresponding acids are produced, since, if an aqueous solution of iodine or bromine is shaken with mercuric oxide, the reactions indicated below take place with the formation of dilute acid solutions.



The latter is especially unstable, decomposing into iodic acid and hydriodic acid:



The bromine compound corresponding to chlorous acid is supposedly prepared by treatment of bromine with concentrated silver nitrate solution.

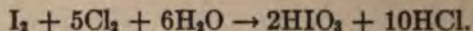


Neither the acid nor its salts have been isolated. The same statement holds for iodosous acid.

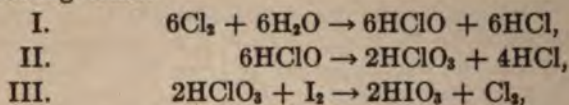
***Bromic and Iodic Acid.*** — If bromine or iodine with water are treated with chlorine the ultimate product of the reaction is



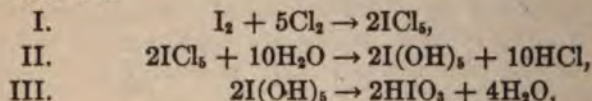
the formation of bromic acid or iodic acid. The reaction may be indicated:



This reaction may be considered as going in three stages by the following route:



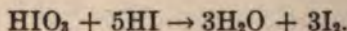
which partial equations by addition give the one above. Or it is possible that



which, being added, give the same summation as before. Which of these courses of reaction actually takes place has not been determined, but both are interesting possibilities.

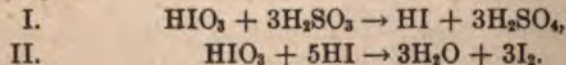
The salts of bromic and iodic acid are readily made by treating hot solutions of the bases with bromine and iodine, the process being entirely analogous with that of chlorine (*q.v.*). Sodium iodate is found in Chile saltpeter and a very considerable portion of the iodine of commerce is obtained from this source (see p. 144).

Bromic and iodic acids are both powerful oxidizing agents, but the latter is less rapidly effective than either chloric or bromic acid. Two interesting cases of its oxidizing property may be mentioned. If iodic acid be added to hydriodic acid the following reaction takes place:



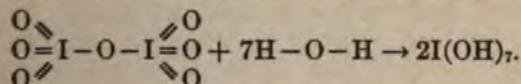
This is reminiscent of the action of sulfuric acid and hydriodic acid (see p. 148).

A very interesting experiment illustrating the oxidizing power of iodic acid is the following: A solution of iodic acid is added to a solution of sulfur dioxide and starch paste in water. A blue color, due to the liberation of iodine, appears after a time interval, the duration of which depends upon the dilution of the solutions employed.

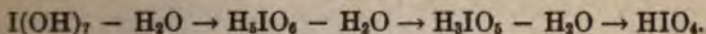


The iodine which is freed colors the starch blue. The blue color cannot appear so long as any sulfurous acid is present because  $\text{H}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4$ . The velocity of a reaction depends upon the concentration of the reacting substances. The greater the concentration of the iodic acid solution the more quickly the reaction I completes itself. The equations I and II may be combined  $2\text{HIO}_3 + 5\text{H}_2\text{SO}_3 \rightarrow \text{I}_2 + 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ .

**Perbromates and Periodates.**—Salts of periodic acid are readily prepared and sodium periodate,  $\text{NaIO}_4$ , is found in small quantities in Chile saltpeter. Neither the corresponding salts of perbromic acid nor the acid itself is known. This is not as is expected from the periodic law (*q.v.*). On the other hand, a somewhat confusing variety of periodates, such as  $\text{AgIO}_4$ ,  $\text{Ag}_3\text{IO}_5$ ,  $\text{Ag}_5\text{IO}_6$ , etc., are known. The existence of such salts may be satisfactorily accounted for by imagining what might take place were iodine heptoxide,  $\text{I}_2\text{O}_7$ , to react with water as indicated below.



If, now, this compound were to lose water one molecule at a time the following compounds would be formed:



While these four forms of periodic acid have not actually been isolated salts of three of them have been produced. Similar acids of other elements are known (*cf.* acids of phosphorus, silicon, etc.). It will be observed that in all these acids the valence of the iodine remains seven. The nomenclature adopted for such cases is illustrated as follows:

- $\text{I}(\text{OH})_7$ , **normal** periodic acid,
- $\text{IO}(\text{OH})_5$ , **para** periodic acid,
- $\text{IO}_2(\text{OH})_3$ , **meso** periodic acid,
- $\text{IO}_3(\text{OH})$ , **meta** periodic acid.

**Fluorine.**—The absence of any mention of oxygen compounds of fluorine may have been observed. The reason is that no such compounds are known. There is also no explanation of this remarkable fact.



**Exercises.** — 1. Describe in detail a method which might be employed to determine that the reaction between chlorine and hot potassium hydroxide produces the chlorate and chloride in the ratio of one formula weight to five.

2. Calculate the volume of chlorine gas, at 15° and 760 mm. pressure, required to saturate 100 cc. of a 10 normal solution of potassium hydroxide if the final products are chlorate and chloride.

3. Write the equations for the successive reactions involved in the production of hypochlorites, chlorates and perchlorates. State the conditions requisite for each change and the energy relations involved.

4. With the principles of reversible reactions in mind, explain in detail Deacon's process and its reversal.

5. How much more heat is liberated in a bleaching action which involves sixteen grams of oxygen when the reaction is carried out by hypochlorous acid than when performed by oxygen itself?

6. If cobalt hydroxide is at 100° an efficient positive catalyzer of the reaction  $2\text{NaClO} \rightarrow 2\text{NaCl} + \text{O}_2$ , how could you prepare oxygen, using sodium hydroxide solution, cobalt chloride and chlorine? Using the method devised, how much oxygen could be prepared from 10 grams of chlorine?

7. At 0° barium chlorate has a solubility of 16.9 grams per 100 cc. and barium chloride of 24 grams per 100 cc. At 20° the corresponding solubilities are 25 and 26 grams. If at 20° a solution is saturated with these salts and cooled to 0°, what is the composition of the precipitate? How would you undertake to prepare pure barium chlorate? If to a solution of barium chlorate saturated at 20° potassium chloride is added, what occurs and to what extent?

8. The solubility of sodium chlorate at 20° is 99 grams per 100 cc. If a saturated solution were treated with potassium chloride, how much potassium chlorate would be precipitated?

9. Formulate the reactions taking place when barium hydroxide is treated with chlorine dioxide.

10. Write structural formulæ for meta and meso periodic acid.

11. Compare the four halogens with respect to valency and to the stability of their compounds.

## CHAPTER XI

### CLASSIFICATION OF THE ELEMENTS

WE have now considered in some detail the chemistry of six elements and have brought into somewhat clear relief the fact that four of these have many properties in common and yet differ in the details of both their appearance and behavior. Yet clearly, if a comprehensive view of all the elements and their compounds is to be gained, without undue waste of space, and of the time of the reader, a systematic classification would aid greatly. Since classification as an aid to comprehension is one of the tools of the scientific trade wherever numerous facts are dealt with, it is not surprising that early efforts to classify the elements were made. The trouble with all the schemes is that whatever property is used as a basis, whether solubility of compounds, valency, or relative basicity or acidity of compounds, the grouping brings together otherwise unrelated elements. In all chemical changes mass remains unchanged, and many attempts have been made to base classifications of the elements upon this property. One of the earliest of these was by Döbereiner (1829), who called attention to the fact that elements related to each other by their chemical behavior consisted either of three elements of nearly the same atomic weights, *e.g.*, iron, 56; nickel, 58.7; cobalt, 59; or that groups of three elements occurred where one had an atomic weight and other properties nearly the mean of the other two. These were called the **triads**. We have just studied one of these groups: Chlorine, 35.46; bromine, 79.92; iodine, 126.92. The mean of 126.92 and 35.46, being 81.19, is almost the atomic weight of bromine. Again, calcium, 40.09; barium, 137.4, give a mean value of 88.74, while strontium, with nearly mean properties, has an atomic weight of 87.5. Other similarly related groups of elements having similar properties were pointed out.

In 1863-6, Newlands in a series of papers called attention to a remarkable regularity observed when the elements were arranged in the order of increasing atomic weights.



H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

Each succeeding eighth element possesses properties relating it to the first (except in the case of hydrogen, which is a sort of Ishmael among the elements and fits into no scheme very satisfactorily) and he proposed to call this relationship the **law of octaves** from its fancied relationship to the musical scale. Newland's work was seriously handicapped by imperfectly known atomic weights and more so because of the fact that certain elements needed for the more satisfactory completion of his scheme were at that time undiscovered. His ideas were unfortunately somewhat pedantically expressed and were received with ridicule rather than belief (though in 1887 he was awarded the Davy Medal for his work).

Nearly the same statements may be made also concerning the work of de Chancourtois, a Frenchman, who in 1862 attempted a rather elaborate effort in the same direction. A more kindly reception attended the efforts of Lothar Meyer, a German, and Mendeleeff, a Russian, who, independently of each other, and probably also of Newlands, in 1869-70, proposed various systems of classification of the elements based on their atomic weights. (For a fuller discussion of the history of this topic see M. Pattison Muir, "Chemical Theories and Laws.")

The most extensively used system of classification is one of those suggested by Mendeleeff. It is ordinarily known as the Mendeleeff Table of the Elements. It is given on the opposite page. In this table are placed also the symbols of certain elements which have been discovered since the first publication of the table. These elements are indicated by italics. Mendeleeff, like Newlands, arranged the elements in the order of their atomic weights **beginning with lithium**. He simply ignored the existence of hydrogen so far as the system is concerned. He was also bold enough, as an examination of the table shows, to assume the existence of undiscovered elements when without such assumption elements unrelated in properties would fall into a group. He was in a way justified in so doing because where such blanks appeared in the table, as between calcium and titanium in series three and between zinc and arsenic in series four, there are abnormally large atomic weight intervals. He also provided the so-called "long periods," series 3 and 4, 5 and 6, 7 and 8, 9 and 10, which are separated into two short series by

Mendeleev's Table of the Elements

	Group 1.	Group 2.	Group 3.	Group 4.	Group 5.	Group 6.	Group 7.	Group 8.
	$RO$ $EA$	$RO$ $EA$	$RO_2$ $EA$	$RO_2$ $RH_2$ $EA$	$RO_2$ $RH_2$ $EA$	$RO_2$ $RH_2$ $EA$	$RO_2$ $RH$ $EA$	$RO_2$ oxides hydrides
Periods								
Short...	1 He	4 Li 6.94	Be 9.1	C 12	N 14	O 16	F 19	
Short...	2 Ne	20.2 Na	Mg 24.3	Si 28.3	P 31	S 32	Cl 35.46	
Long...	3 Ar	39.9 K	Ca 40.1	Sc 44.1	Ti 48.1	V 51	Cr 52.0	Fe 55.9, Ni 58.7, Co 59
Long...	4 Kr	82.9 Rb	85.5 Sr	Y 89	Zr 90.6	Nb 93.5	Mo 96	Ru 101.7, Rh 103, Pd 106.7
Long...	6 Xe	131.3 Ba	137.4 La	Ce 140.3	Pr 140.9	Nd 144.2	Pm 145	
Long...	8 Rn	222.0 Po	210	209	209	209	209	
Long...	10 Fr	223.0 Ac	227.0 Th	232.0 Pa	231.0 U	238.0 Np	237.0 Pu	
Short...	11 At	210	210	210	210	210	210	



groups of three elements of like properties. In a few cases he ignored the actual order of the atomic weights, preferring to assume the weights as determined to be incorrect. This apparent neglect of facts he justified, since when so arranged elements of like properties fell into the same group. For a very satisfactory presentation of the matter the student is referred to Mendeleeff's Chemistry, Vol. II, pp. 1-25. The student should note that the zero group was unknown and its existence unsuspected by Mendeleeff (see Chapter XV). In the table as given we have nine vertical columns of groups of elements the members of which possess like properties. Each group may be regarded as consisting of a type element and two sub-groups *A* and *B*. The members of each sub-group are usually closely related and resemble less clearly the members of the other sub-group. Concerning this remarkable relation between the atomic weights of the elements Mendeleeff says: "When I arranged the elements according to the magnitude of their atomic weights, it became evident that there exists a kind of periodicity in their properties, and I designate by the name 'Periodic Law' the mutual relation between the properties of the elements and their atomic weights. . . . These relations have the nature of a periodic function." This is commonly more concisely expressed: **The properties of the elements are a periodic function of their atomic weights.** This is usually called the periodic law, but it is more properly to be regarded as a formulative hypothesis in that we assign to the atomic weight a causal relation to the properties.

It is not to be supposed that this classification is the "*dernier cri*" on the subject. Indeed, many others have attempted classifications of a similar type. We have the helix of Story, the descending figure eight of Crooks, and many others. In Chapter XXXVI we shall present some points concerning the modern system of Harkins. On the whole, however, we shall find the table given very useful and shall base our order of discussion upon it.

**Uses of the Periodic System.** — 1. The periodic system serves as a basis of classification which brings together elements of similar properties. Such arrangement facilitates both the understanding and the recollection of the characteristic properties of the elements. While this system is, as we shall see, not ideal, it is perhaps better than any other at present available.

2. The periodic system aids in the selection of the equivalent

weights which are best suited for use as the atomic weights of the elements. Such selection is not always easy. Certain elements furnish no volatile compounds (*cf.* Chap. V) and some no soluble compounds (*cf.* Chap. X). In other cases special difficulties arise. Two examples will serve to show how the periodic system is an aid. Radium was not, for some time after its discovery, prepared in sufficiently large quantities so that its atomic weight could be readily determined. The analysis of its bromide gives an equivalent weight of 113.2. The general chemical properties of radium are distinctly like those of barium. Its atomic weight is therefore 226.4 and the formula  $\text{RaBr}_2$ . This atomic weight places radium in group II and series II. Its properties accord fully with this position (*cf.* Radium, p. 464). Again: The equivalent weight of indium was shown by Winkler to be 37.8. Its atomic weight is therefore some multiple of this number. Should we choose 75.6 ( $2 \times 37.8$ ), the element would come in the periodic system between arsenic and selenium instead of in the group of elements with like properties. If, however, we select 113.4 ( $3 \times 37.8$ ) it places the element in group three, series six, where it fits. Mendeleeff himself suggested this choice for indium and subsequent investigation of its specific heat (0.0577) and more exact determination of the equivalent weight give us the atomic weight 114.2. A very considerable number of atomic weights have been selected using the periodic system as a basis of choice.

3. According to Mendeleeff, the blank spaces in his system were due to the existence of elements as yet undiscovered. This seemed to him so certain that he predicted the properties of several elements, these predictions being based upon the places in groups and series which could be filled by elements of given atomic weights. His predictions were made in great detail for some elements and their marvelous accuracy was no small factor in establishing the system. A comparison between predicted properties and those found is shown below. The possibility of prediction on the basis of the system is not limited to undiscovered elements. There are many instances on record in which consideration of the places of elements in the system have led to investigations which resulted in the discovery of new compounds. There yet remain many possibilities of utilization of the table in this manner. One unexpected result of this aspect of the system is the publication of "faked" reports. One of the most notable of these is the investigation of Ogawa, a Japanese (*Jour. Lond. Chem. Soc.*, **94**, 952). He reports full



confirmation of the prophecies of Mendeleeff regarding eka-manganese which should occupy the vacant space in series 5, group 7.

Eka-silicon.	Germanium (Winkler).	Eka-aluminium.	Gallium (de Boisbaudran).
Predicted, 1871 Atomic wt., 72 Specific gr., 5.5	Discovered, 1886 Atomic wt., 72.3 Specific gr., 5.47	Predicted, 1871 Atomic wt., 69 Will have a low melting point	Discovered, 1875 Atomic wt., 69.9 Melting point, 30.15°
Dirty gray with white oxide, $\text{EsO}$ Atomic volume, 13	Dirty gray with oxide, $\text{GeO}$ Atomic volume, 13.2	Will not be oxidized in air The oxide will be $\text{El}_2\text{O}_3$	Only slightly oxidized at red heat The oxide is $\text{Ga}_2\text{O}_3$
Element decomposes steam with difficulty	Element does not decompose steam	Will decompose water at red heat	Decomposes water at red heat
Acids react slightly	Not attacked by $\text{HCl}$ nor solutions of $\text{KOH}$	The chloride will be $\text{El}_2\text{Cl}_3$	The chloride, $\text{Ga}_2\text{Cl}_3$
Alkalies, no pronounced action	Oxidized by fused $\text{KOH}$	Sulfate, $\text{El}_2(\text{SO}_4)_3$	Sulfate, $\text{Ga}_2(\text{SO}_4)_3$
Action of sodium on the oxide or $\text{K}_2\text{EsF}_6$ will give the metal	Germanium prepared by reduction of oxide by carbon or $\text{K}_2\text{GeF}_6$ by sodium	Will form an alum. Will be easily reduced by electrolysis. May be expected to be discovered by the spectroscope	Forms an alum. Easily obtained by electrolysis. Was discovered by the spectroscope
The oxide, $\text{EsO}_2$ , will be refractory with sp. gr. 4.7.	Oxide, $\text{GeO}_2$ , refractory with sp. gr. 4.703		
Basic properties less marked than those of $\text{TiO}_2$ .	Basicity very feeble		
Chloride $\text{EsCl}_4$ will be a liquid, sp. gr., 1.9. Boiling point a little below 100°.	The chloride, $\text{GeCl}_4$ , is a liquid, sp. gr., 1.88. Boiling point, 86°.		
The ethide, $\text{Es}(\text{C}_2\text{H}_5)_4$ , will be a liquid, sp. gr., 0.96 and b. p., 160°	The ethide, $\text{Ge}(\text{C}_2\text{H}_5)_4$ , is a liquid with b. p., 160°. Sp. gr. slightly less than water.		
The fluoride, $\text{EsF}_4$ , will not be gaseous	The fluoride, $\text{GeF}_4$ , is a solid		

Sir William Ramsay and R. B. Moore in separate investigations failed to confirm the results. Ogawa proposed to call the new ele-

ment nipponium (Nippon = Japan), thus following the example set by Nilson, de Boisbaudran and Winkler in naming scandium, gallium and germanium after their respective countries.

**Defects in the Periodic System.**—There are various places in the system of Mendeleeff where the classification is unsatisfactory, especially if the arrangement in order of atomic weights is rigidly followed. The atomic weight of iodine is 126.9, while that of tellurium is 127.5. These values place iodine in a group with oxygen and sulfur, and tellurium in the halogen group. The properties of these elements call for reversed positions. The explanation offered by Mendeleeff is that the **correct** atomic weight of tellurium is probably about 125. The most strenuous efforts of several chemists have failed to justify this atomic weight. Flint (Am. Jour. Sci., 30, 1209, 1910) claims to have obtained atomic weight values for tellurium of 124.3, but his results have failed of confirmation by others. Another case is furnished by argon (at. wt., 39.9) and potassium (at. wt., 39.1). Their properties call for the positions given them in the table (*q.v.*). Again the rare earths (*q.v.*) are fitted into the Mendeleeff table only with difficulty. Indeed, these elements offer serious difficulties in any system which has been suggested (*cf.* Chap. XXXVI).

The most serious defect of the system, so far as its general utility is concerned, is that elements which are chemically similar are not always brought together by the table. This failure is especially evident in qualitative analysis, where elements of unlike periodic position are brought into close relation. Also, copper and mercury have many similar properties and no indication of this similarity is indicated by the table.

The fact that hydrogen finds no place in the table is, of course, a defect in the system. No very satisfactory explanation is at hand. One of the many assumptions is that there probably exists a zero series of which hydrogen is the first member. This assumption is not based upon experimental evidence. The most interesting effort to eliminate this and similar defects of the system is that of Harkins and is based on a unitary theory of matter (*cf.* Chap. XXXVI).

These difficulties in the system and the attempt to consider the system as dependent upon an established law have led certain chemists to regard the various systems as merely "catalogues" of the elements. It is perhaps better to regard the present difficulties as probably due to lack of sufficiently exact and detailed



knowledge and to regard the systems as based upon the **periodic hypothesis**.

*Exercises.* — 1. Why is the atomic weight taken as the fundamental property in the statement of the periodic law?

2. Make a list of six sets of triads and show that the element of mean atomic weight has mean properties.

3. Calculate the mean difference between the atomic weights of the first two series of elements. Assuming that such mean holds approximately, what is the atomic weight of the element corresponding to the blank in series 5?

4. Indicate in what respects the periodic law is hypothetical.

5. An element is discovered having compounds very similar to those of manganese. Its chloride is analyzed and its equivalent is found to be 49.4. What is the atomic weight? Why?

6. An element may be found having an atomic weight of 61.3. What ought to be its properties?

7. In view of the fact that radium, thorium and uranium are constantly decomposing, what may be the reason for the blank in series 11, group 7?

8. If the periodic system as given is used as a guide, should the element corresponding to the blank in series 8, group 7, be discovered, what properties would it have?

## CHAPTER XII

### SULFUR AND ITS COMPOUNDS

#### SELENIUM AND TELLURIUM

THE compounds of sulfur and those of oxygen present many points in common and where divergence of a marked kind is found we are able to assign graphic formulæ which indicate a higher valence of sulfur than is exhibited by oxygen and to which the variation is presumably due. From time to time analogies will be pointed out and the student is urged to find others for himself, and also to look for other than "family" traits of character as they may become evident.

**Occurrence.** — Sulfur is found in great abundance and variety of forms. Free, it occurs in two types. **Volcanic sulfur**, deposited from gases of volcanic origin, is ordinarily mixed with more or less volcanic ash. Deposits are found in practically all volcanic regions, *e.g.*, Japan, Mexico, Iceland, Italy, Greece, etc. **Sedimentary sulfur**, probably produced by decomposition of deposits of calcium sulfate, is found in large deposits. The sulfur deposits of Sicily and those of Texas are of this type (*cf.* preparation, p. 214). Combined, sulfur is found in mineral forms chiefly as sulfides and sulfates. The more important sulfides, so far as quantity is concerned, are iron pyrites,  $\text{FeS}_2$ , galena,  $\text{PbS}$ , and zinc blende,  $\text{ZnS}$ . Other sulfides are important ores of the metals with which the sulfur is associated. Examples are: **Orpiment** and **realgar**, ores of arsenic; **chalcocite**, **chalcopyrite** and **bornite**, ores of copper; **smaltite**, an ore of cobalt and nickel; **stibnite** an ore of antimony, etc. The more abundant sulfates are: Gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Glauber's salts,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Sulfur is an essential constituent of all albuminous material. It is also a constituent of many anabolic and metabolic products of animal and plant organisms.

**History.** — Sulfur was known to the ancients and its discovery dates to a prehistoric period. It is mentioned both in Job and



Genesis and apparently the word translated "brimstone" refers both to the element and to sulfur dioxide, Hell being described in the Revelations (14, 10; 19, 20; 20, 10) as a lake of fire and brimstone and hence with an atmosphere of sulfur dioxide, presumably. The substance is also mentioned by Homer and by Pliny. Dioscorides apparently knew both the ordinary and amorphous varieties. For the alchemists sulfur was of such importance that it was considered one of their three fundamental elements, probably representing the factor of combustibility. Milk of sulfur was known to the Arabian physician Geber (from whom we, unjustly, derive the name gibberish). Monoclinic sulfur was first recognized by Mitscherlich in 1823. The various kinds and crystalline modifications of sulfur have been the subject of an enormous number of investigations and the literature is very voluminous. Only an outline of the better known varieties is presented here.

**Preparation.**—Sulfur which is obtained directly from the Louisiana and Texas deposits is about 99.5% pure. The mining

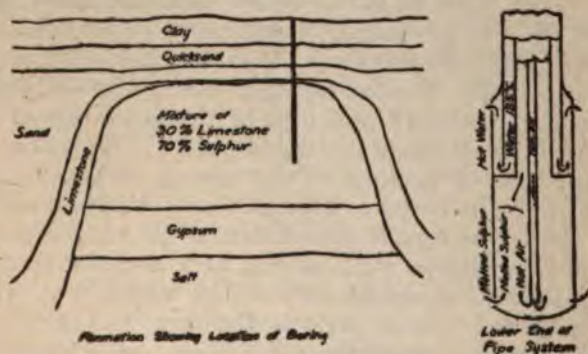


FIG. 56.

process is itself a method of purification. Wells are drilled into the sulfur stratum, which is 500 feet or more beneath the surface. These wells are cased and superheated steam is forced into them. The sulfur, being melted by the steam, is either pumped or forced to the surface in liquid form. (See Fig. 56.) In 1913 about 475,000 tons of sulfur were produced in this manner. Sulfur is freed from admixed volcanic ash by heating to a temperature sufficient to liquefy the sulfur. It is then allowed to run into

wooden molds to solidify. The sulfur so obtained is known as **brimstone**. To obtain pure sulfur the brimstone is distilled in earthenware retorts and the vapor condensed in brick chambers. The sulfur vapor at first deposits as a light yellow solid, without first becoming liquid (sublimation). This deposit is called "flowers of sulfur." As the chamber warms somewhat the vapors condense to liquid sulfur, which is run into molds. This is sold as pure "roll sulfur."

Some sulfur is also manufactured from iron pyrites by heating,  $3\text{FeS}_2 \rightarrow \text{Fe}_3\text{S}_4 + \text{S}_2$ ; some as a by-product in the Le Blanc soda process (*q.v.*) and some also as a by-product from gas purification (*q.v.*).

Sulfur for medicinal purposes is manufactured from polysulfides (*q.v.*) by treatment with acids. This is known as precipitated sulfur and before the Food and Drugs Act came into operation was frequently grossly adulterated.

**Physical Properties of Sulfur.** — Several varieties of sulfur may be prepared, hence sulfur is said to be polymorphous ( $\pi\omicron\lambda\acute{\upsilon}\varsigma$  = many and  $\mu\omicron\rho\phi\acute{\eta}$  = form). These modifications are in some cases due to differences in crystalline form and in other cases are allotropic. The latter term is used to describe modifications of elements which differ in physical and chemical behavior and in the energy relations involved in their transformations and in which these differences cannot be satisfactorily assigned to changes in form only. We have already encountered an instance of allotropy in the relation between oxygen and ozone. We shall later meet many other instances (*vide* phosphorus, carbon, silicon, etc.). Three varieties of sulfur will be briefly described. (For a somewhat more extended discussion see Mellor's *Modern Inorganic Chemistry*, p. 395, *et seq.*).

**Crystals and Crystal Systems.** — When a liquid solidifies it frequently changes into more or less clearly defined bodies. These are known as crystals. Crystals may be deposited from solutions by cooling or evaporation and also by the cooling of vapors. They may be so closely interwoven as to render indistinct the shape of the individual bodies and in such case the solid mass is said to be **crystalline**. Crystals present definite plane surfaces which are arranged in an orderly fashion with respect to each other. The crystal form of a substance is always characteristic. The number of crystal forms is very great and yet if we imagine each crystal to possess certain axes all crystals may be classified into six systems. The study of these systems and the relation of crys-



tals to them is the subject of crystallography. (See Moses and Parsons' Mineralogy, Part 1.) Below are given the names of the six systems, together with the relation of the imaginary axes to each other. In the figures are given outline drawings of simple examples of each system, showing the relation of surface planes to the axes.

1. **The isometric or regular system.** — This system possesses three axes of equal length at right angles to each other (Fig. 57).

2. **The tetragonal system** possesses two axes of equal length and one of a different length all at right angles to each other (Fig. 58).

3. **The orthorhombic, or rhombic system** has three axes of unequal length all at right angles to each other (Fig. 59).



FIG. 57.

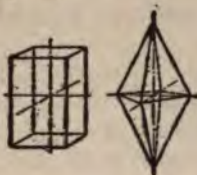


FIG. 58.

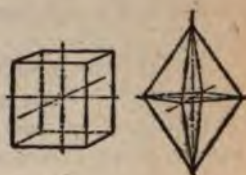


FIG. 59.

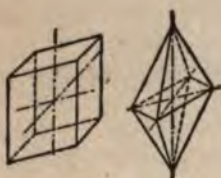


FIG. 60.



FIG. 61.

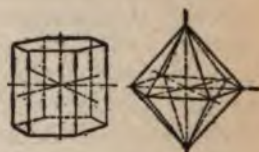


FIG. 62.

4. **The monoclinic system** has two axes at right angles and a third which is at a right angle to one of these but is inclined toward the other. The axes may vary in length (Fig. 60).

5. **The triclinic system** has three axes all inclined toward each other and of variable length and inclination (Fig. 61).

6. **The hexagonal system** has three equal axes in the same plane at angles of  $60^\circ$  to each other with a fourth at right angles to all the others (Fig. 62).

These systems unquestionably correspond to an orderly arrangement of the molecules and depend on the form of the molecules themselves. Each substance, therefore, ordinarily crystallizes in forms which can all be referred to one of the above systems. The actual forms may, however, be quite varied. Crystals seldom exhibit complete geometrical forms, that is to say the complete architectural design is rarely completed, yet the internal structure is always characteristic and by means of optical properties and the cleavage planes produced by fracture of the crystal this structure may be recognized. Occasionally substances

are observed to crystallize in different forms which must be referred to more than one system. Sulfur is an example of such a substance. If two systems are represented the substance is said to be **dimorphous**. If more than two it is **polymorphous**. Occasionally different substances crystallize in the same form and are hence called **isomorphous**. (See Mitscherlich's Law of Isomorphism.)

**Rhombic Sulfur.** — As sulfur is ordinarily encountered, it is pale yellow, brittle, tasteless, odorless, and insoluble in water. It consists of minute imperfect crystals, which are classed by the crystallographers as rhombic. If sulfur be dissolved in carbon disulfide and the solution slowly evaporated spontaneously, large octahedral crystals may be obtained. About thirty varieties of such crystals, all of the rhombic type, have been described. Sulfur in this form has a specific gravity of from 2.06 to 2.03. It is soluble to varying degrees in solvents, such as chloroform, essential oils, glycerine, alcohol, etc. About 70% of flowers of sulfur is of this type. Its melting point is 112.8°.

**Monoclinic Sulfur.** — If a fairly large quantity of sulfur is melted and allowed to cool until a surface crust is formed, the surface may be punctured and the portion yet liquid may be poured out. The crust may be removed and the interior found partially filled with long needle-shaped crystals of the monoclinic type. This form of sulfur differs from rhombic sulfur in many respects. The specific gravity is 1.93. The melting point is 119.5°. The monoclinic form slowly changes to the rhombic form at ordinary temperature. This change is of course accompanied by change of volume since the specific gravity changes from 1.93 to 2.06. By means of a dilatometer (see Fig. 63) this change of volume may be measured. Thus, if crystals of the monoclinic type are placed in the bulb and the vessel is filled to the mark *A* with a suitable liquid the change of volume may be noted by the lowering of the liquid level. Also, by means of the dilatometer it may be shown that both forms are stable in the

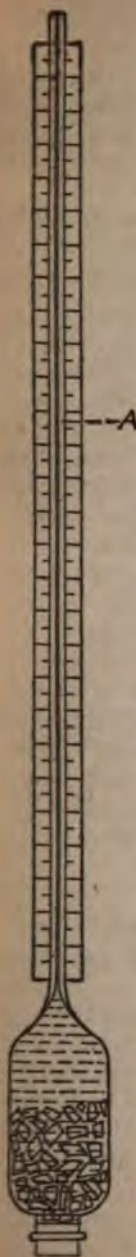


FIG. 63.



presence of each other at 94.5°. This temperature is known as the transition temperature. Above 94.5° rhombic changes to monoclinic; below, monoclinic to rhombic. There are several varieties of crystals of the monoclinic type.

**Amorphous Sulfur.** — If sulfur be heated to just above its melting point it forms a straw-colored, limpid liquid. If it be heated slowly to a higher temperature it gradually darkens and becomes more viscous. At 162° it is almost black and will no longer pour from the containing vessel. This viscosity reaches a maximum at 180°. As the temperature is raised the liquid, though remaining dark, becomes again mobile. The boiling point is 444.5°. If sulfur at a fairly high temperature, about 350°, is poured into cold water it solidifies to a tough rubbery mass which gradually hardens. The hardened sulfur is only partially soluble in carbon disulfide. It thus appears that molten sulfur consists of at least two varieties. They are known as  $\lambda$ -sulfur and  $\mu$ -sulfur. These two varieties of sulfur are not crystalline and are hence called amorphous. The amorphous  $\lambda$ -sulfur may also be produced by treating a saturated solution of sulfur dioxide, at 0°, with hydrogen sulfide:  $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 3\text{S}$ . This variety of sulfur is nearly pure white and is wholly soluble in carbon disulfide. If, however, a solution of a polysulfide (*q.v.*) is treated with a dilute acid, a finely divided suspension is obtained, which is known as **milk of sulfur**. The suspended sulfur will slowly settle out. It is the non-crystalline  $\mu$  sulfur. It is almost wholly insoluble in carbon disulfide. It slowly changes to rhombic sulfur on standing.

**Chemical Properties.** — Sulfur combines slowly with the oxygen of the air at ordinary temperature, in the presence of moisture. The product of the reaction is sulfur dioxide,  $\text{SO}_2$ . The kindling point in air is about 363°. It kindles at a lower temperature in oxygen and as a vapor in both air and oxygen. The product of burning sulfur is mainly sulfur dioxide. If sulfur is brought into intimate contact with metals sulfides are often produced; in some cases at the ordinary temperatures in other cases only at elevated temperature (*cf.* mercury and sulfur, p. 41, and iron and sulfur, p. 12). At a high temperature it combines directly, though slowly, with carbon, chlorine and hydrogen (*vide infra*). It will be observed therefore that sulfur is a very active element.

This chemical activity is, however, less obvious than in the case of oxygen, because sulfur is a solid and intimacy of contact between it and other elements is less readily secured.

If sulfur is treated with powerful oxidizing agents, e.g., with concentrated nitric acid, in the presence of water the product of the reaction is sulfur trioxide,  $\text{SO}_3$ . The sulfur trioxide with water forms sulfuric acid,  $\text{H}_2\text{SO}_4$ .

The specific gravity of sulfur vapor at  $500^\circ$  is approximately 6.6, which corresponds to a molecular weight of 181, or  $\text{S}_8$ . As the temperature of the vapor is increased the density decreases until at  $1000^\circ$  it corresponds almost exactly to the formula  $\text{S}_2$ . Above  $1000^\circ$  the density remains quite constant until  $1700^\circ$  is reached, when it begins again to decrease with increasing temperature. (Cf. iodine, p. 145.) The molecular weight of sulfur as determined in solution by the freezing and boiling point methods is 256, or  $\text{S}_8$ . It would appear, therefore, that according to the temperature we may have a molecular complexity of  $\text{S}_2$ ,  $\text{S}_4$ ,  $\text{S}_6$ , or  $\text{S}_8$ . Whether in fact molecules corresponding to  $\text{S}_4$  exist is not definitely ascertained, since a mixture of  $\text{S}_2$  and  $\text{S}_8$  in proper proportions might give densities corresponding to either  $\text{S}_4$  or  $\text{S}_6$ .

A substance showing the minimum quantity of sulfur in a gram molecular volume is hydrogen sulfide, which consists of 2.016 parts of hydrogen and 32.06 parts of sulfur. The atomic weight of sulfur is therefore 32.06. The equivalent weight of sulfur in silver sulfide as determined by Stas is 16.035. Sulfur is therefore bivalent in compounds of this type. As we shall see, sulfur may also manifest a valency of either four or six as illustrated by the two oxides,  $\text{SO}_2$  and  $\text{SO}_3$ .

**Uses.**—Sulfur finds extensive application in the manufacture of gunpowder, matches, vulcanized rubber, color materials, sulfite liquors for bleaching, sulfur dioxide for disinfection and for sulfuric acid, sulfur compounds used as insecticides and fungicides, etc. It is also used both as an element and in compounds for various medical purposes. An indication of the quantity used is shown by the fact that in the United States about 300,000 tons were consumed in 1915.

#### HYDROGEN SULFIDE AND DERIVATIVES

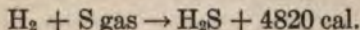
**Occurrence.**—Hydrogen sulfide occurs as a free gas in the exhalations from volcanoes and is found in small quantities dis-



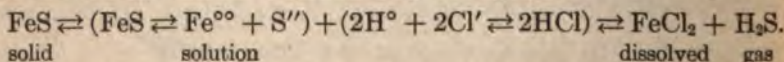
solved in certain mineral waters, where it is usually produced by the hydrolysis of mineral sulfides. It and its organic derivatives are also formed during the decay of albuminous material in absence of air. It is, therefore, a component of the ill-smelling gases arising from sewers and in harbors. It is consequently present in the air of cities. Its salts, the sulfides, are extremely abundant in nature and are widely distributed (*cf.* p. 213).

**History.** — Since milk of sulfur was known to the alchemists, they must have also known the odor of hydrogen sulfide, since it is formed in the same reaction. Indeed, Boyle, 1663, knew that the gas "blackened silver just as liver of sulfur does." Meyer of Osnabruck (1764) knew the gas to be combustible and that it is poisonous. Yet the first careful investigation of its properties was published in 1777 by Scheele in the same paper in which he announced the discovery of oxygen. He gave it the highly descriptive, though not elegant, name of "stinking sulfur air." It was given the name hydrogen sulfide by Gengembre in 1785. Its use in chemical analysis was first advised by Fourcroy in 1787 and its complete recognition as a non-oxygen acid established by Berthollet in 1786.

**Preparation.** — 1. Hydrogen and sulfur combine directly, with appreciable rapidity, only at elevated temperature — as by passing the two substances in the form of gases through a red hot tube or by bubbling hydrogen through sulfur kept near its boiling point.

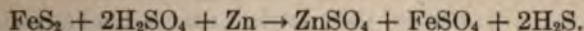


2. The most convenient method of preparation is to treat a sulfide, such as FeS, ZnS, Na<sub>2</sub>S, etc., with a dilute acid, which is not at the same time an oxidizing agent. Of course, we must assume in terms of the ionization hypothesis that the reaction only occurs between the soluble sulfide and acid. If, then, only a moderately soluble sulfide is used, the rate of reaction will, in part, be determined by the rate of solution and hence the speed of reaction be more easily controlled. We are then dealing with both sorts of equilibria (p. 133 *et seq.*) and the reaction may be expressed:

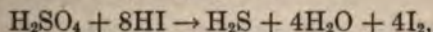


The reaction goes to completion both because the gas H<sub>2</sub>S is but slightly soluble and because it is only slightly ionized. Of course,

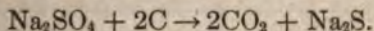
any soluble sulfide can be used in lieu of ferrous sulfide, but because of its cheapness and the comparative ease with which the rate of flow may be regulated by means of a Kipp apparatus the ferrous sulfide is ordinarily employed. Insoluble sulfides of the type of iron pyrites are not acted upon by acids with appreciable rapidity, but by simultaneous action of nascent hydrogen and acid are reduced, *e.g.*, if zinc and iron pyrites are mixed and treated with acid:



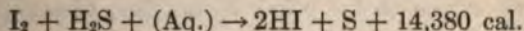
3. Hydrogen sulfide is also produced when sulfuric acid is treated with powerful reducing agents:



and in an analogous manner all sulfates are, by sufficiently active reduction, reduced to sulfides. Thus, with a blowpipe on charcoal



Indeed, by reduction of sulfur itself, hydrogen sulfide may be produced. Thus, by heating sulfur and hydriodic acid we obtain:  $2\text{HI} + \text{S} \rightarrow \text{H}_2\text{S} + \text{I}_2$ . This reaction is a reversal, so far as form is concerned, of that given on p. 150, but the conditions are such that the energy relations are very different. The heat of formation of gaseous HI at 18° C. is - 6100 cal. Therefore  $2\text{HI} + \text{S} \rightarrow \text{H}_2\text{S} + \text{I}_2 + 10,920$  cal. The heat of formation of aqueous HI is 19,200 cal. Therefore an aqueous suspension of  $\text{I}_2$ , with hydrogen sulfide reacts:



Both reactions, therefore, are exothermal and hence not true reversals of each other.

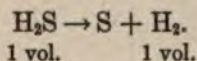
4. Certain sulfides suffer complete hydrolysis in water and hence may be used for the preparation of hydrogen sulfide. An example is  $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{S}$ . It is obvious that such sulfides may not be formed in aqueous solution.

**Physical Properties.**—Hydrogen sulfide is a colorless gas which has an odor "reminiscent" of spoiled eggs, which, indeed, owe a portion of their odor to this gas. The odor is usually classed as unpleasant, but like the trite quotation concerning vice, with familiarity one gets into a frame of mind which approaches appreciation. It liquefies under pressure to a colorless fluid with a boiling point of about -62°. Its critical temperature is 100° C.



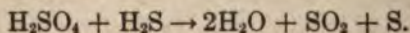
It dissolves in water: 437 vol. to 100 vol. at 10° C. The gas is poisonous and even when diluted with much air its inhalation produces headache and, if continued, nausea and coma, and ultimately death. Inhalation in concentrated form produces serious symptoms at once. Sewer gas poisoning is largely due to hydrogen sulfide. The gas has a specific gravity of 1.1912.

**Chemical Properties.** — The chemical properties of the gas are very important because of their typical nature, and also because of the extensive use of the substance as a reagent. Its specific gravity as a gas corresponds to a molecular weight of 34, and its analysis calls for the exact weight 34.09. The volume relations are shown by decomposition through sparking a measured amount in a tube over mercury, or by allowing it to stand over tin which is supported by a mercury column. The resulting volume of hydrogen is the same essentially as that of the original gas. The volume of the solid sulfur is negligible, hence we may write the molecular equation:



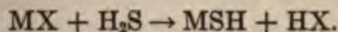
The gas burns in air:  $\text{H}_2\text{S} + 3\text{O} \rightarrow \text{H}_2\text{O} + \text{SO}_2$ , but if a cold vessel is plunged into the burning gas and removed it will be found coated with a deposit of sulfur. This may be considered as indicating that  $2\text{H}_2 + \text{S}_2 \rightleftharpoons 2\text{H}_2\text{S}$  is a reversible reaction and that at high temperature there is a considerable proportion of free sulfur in the unburned gas, which cooled below its kindling temperature by the cold surface is, therefore, deposited.

The gas reacts readily, even at ordinary temperatures, on the metals of the electromotive series down to and including silver, producing sulfides. This is like the behavior of sulfur and is probably due to the presence of sulfur as indicated by the above equilibrium system. The behavior of the gas with sulfur dioxide also indicates its instability, since  $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ . It is true this reaction may be due to the presence of moisture and belong to the reducing effects of the acid solution (see below). Volcanic sulfur is supposed to be produced by this means, both gases being produced by volcanic action. If we attempt to dry the gas by means of concentrated sulfuric acid we find that it and the acid are decomposed:

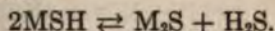


We must, therefore, use some non-oxidizing (and as we shall see, non-basic) drying agent; the most convenient one for the purpose is phosphorus pentoxide. The solution of hydrogen sulfide in water is called, when the object is to emphasize its acid nature, hydrosulfuric acid, and its most important properties may be classed under three heads.

1. **Acid Action.**—The aqueous solution of hydrogen sulfide is a very weak acid (*cf.* p. 175). The ions are apparently  $H^+$  and  $SH^-$ . The equilibrium may be represented,  $H_2S \rightleftharpoons H^+ + SH^-$ . This is similar to the ionization of water. The solution also reacts as a dibasic acid and furnishes both neutral and acid salts. So far in our discussion of acids attention has been directed chiefly to the hydrogen ion. In the present instance the anion is the more important. This is because the salts are of extensive use in analytical operations because of their varied behavior. We may indicate the general behavior of solutions of the salts of metals by the following equation:



With many metals the hydrosulfide is unstable and produces the sulfide by decomposition:

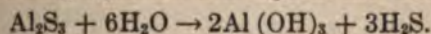


If the sulfide is insoluble it will precipitate and both reactions go to completion in the direction  $\rightarrow$ . The various metal sulfides may be divided into five groups:

1. Sulfides which are precipitated in insoluble form by hydrogen sulfide from salt solutions even in the presence of an excess of acid. These are the sulfides of silver, lead, mercury, bismuth, copper, cadmium, arsenic, tin, antimony, and of certain of the rarer elements. These sulfides are of two sorts; *A*, those insoluble in alkaline sulfides and *B*, those soluble in alkaline sulfides. To the latter sort belong arsenic sulfide, antimony sulfide, and tin sulfide.

2. Sulfides which are insoluble when in neutral solution but are not precipitated in the presence of acids. To this group belong such sulfides as those of iron, cobalt, nickel, manganese and zinc.

3. Sulfides which while they form in aqueous solution are hydrolyzed by water giving insoluble hydroxides. Such are the sulfides of aluminium, chromium and of iron when in the ferric state. The following equation will explain the reaction:



↓

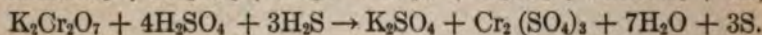
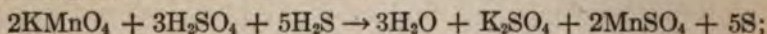


4. Sulfides which are hydrolyzed by water but produce hydroxides sufficiently soluble to remain in solutions of reasonable dilution. Examples are the sulfides of barium, strontium and calcium.

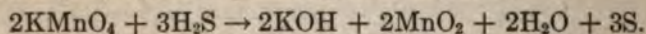
5. Sulfides fairly stable in aqueous solution. Examples are sulfides of sodium, potassium and ammonium.

The sulfides not only differ in solubility, as indicated by the above grouping, but the members of each group differ from each other in color and degrees of solubility to an extent which renders them very useful as a means of detecting the presence of metals. The use of hydrogen sulfide for the purpose is so extensive that the odor of the gas may be said to be characteristic of an analytical laboratory.

**2. Reducing Action.** — The second property of hydrogen sulfide which makes for utility is its reducing power. When we treat solutions of ordinary oxidizing agents with hydrogen sulfide we get immediate reduction and at room temperatures. Thus acidified permanganates react as indicated:

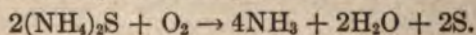


Hydrogen sulfide also acts as a reducing agent in neutral or alkaline solution, but the products of the reaction may be different. Thus in the case of permanganate we have:



**3. Instability.** — The instability of hydrogen sulfide as a gas has been mentioned (p. 222). In solution it is also unstable. Indeed the reducing power of the solution is probably due to its instability. If aqueous solutions of the gas are exposed to the air the gas not only escapes but a part decomposes by reaction with oxygen:  $2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{S}$ . Sunlight also facilitates the decomposition. Solutions of the gas are therefore not readily kept and this fact, coupled with its relatively small solubility, accounts for the use of hydrogen sulfide in gaseous form. The gas is manufactured and passed into solutions in which it is expected to function.

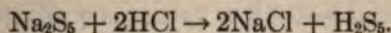
The oxidizing effect of air and also the effect of sunlight operate, though to a lesser degree, upon solutions of the soluble sulfides. In consequence the extensively used reagent, ammonium sulfide,  $(\text{NH}_4)_2\text{S}$ , is kept in closely stoppered brown bottles to minimize the tendency to decompose as indicated:



Fuller discussion of certain sulfides will appear as the metals themselves come up for review. (See also texts on Qualitative Analysis.)

**Polysulfides.** — Just as oxygen forms two oxides with hydrogen, so sulfur. When sulfur is shaken with a solution of an alkaline sulfide it dissolves and if the solution is evaporated the residue has a composition which varies between the limits  $\text{Na}_2\text{S}_2$  and  $\text{Na}_2\text{S}_5$ , according to the amount of free sulfur used.

If this material be dissolved in water and poured into a weakly acid solution, a yellow oil separates. This is perhaps according to the following equation:



If this oil be distilled under diminished pressure it may be resolved into fractions which by the freezing point method may be shown to correspond to the formulas  $\text{H}_2\text{S}_2$ ,  $\text{H}_2\text{S}_3$ , and  $\text{H}_2\text{S}_5$ . If the reverse order is followed and the acid is poured into the alkaline sulfide, the reaction takes place as indicated:  $\text{Na}_2\text{S}_5 + 2\text{HCl} \rightarrow 2\text{NaCl} + 4\text{S} + \text{H}_2\text{S}$ . The first of the compounds above mentioned is very unstable and its behavior relates itself closely to that of hydrogen peroxide. The others will be again mentioned under the topic of constitution of sulfur compounds. The soluble salts of these compounds with metals are jointly known as the **polysulfides**. The most important polysulfide is perhaps that known as yellow ammonium sulfide  $(\text{NH}_4)_2\text{S}_x$ , which is much used as a laboratory reagent. Another extensively used polysulfide is that of calcium,  $\text{CaS}_x$ , which under various trade names is extensively used as a germicide, fungicide and insecticide.

### SULFUR DIOXIDE

**Occurrence.** — This oxide is found in nature in volcanic gases and in springs in volcanic regions and is always present in the air of cities where coal containing sulfur is burned.

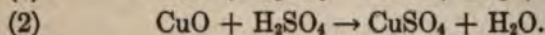
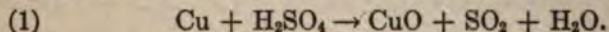
**History.** — Sulfur dioxide was used in the time of Homer as a disinfectant and in religious ceremonies. Its bleaching powers were known to Paracelsus. Von Helmont knew that the gas would quench flames. Its solution in water was for long confused with sulfuric acid. Priestley obtained the gas by reduction of



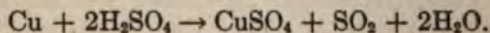
sulfuric acid and called it vitriolic acid air. In 1777, Lavoisier demonstrated its relation, when dissolved in water, to sulfuric acid and hence in accord with his system of nomenclature he called it sulfurous acid.

**Preparation.** — 1. When sulfur is burned either in air or oxygen, the chief product is the dioxide, with small amounts of sulfur trioxide. Sulfur dioxide is also formed by oxidation of sulfur with certain oxidizing agents, though the trioxide is ordinarily formed. It may also be formed by roasting, *i.e.*, heating in air, of iron pyrites and of other sulfides. This method, essentially burning sulfur, is the one commonly employed for its preparation on a large scale, and makes it a by-product of many metallurgical processes.

2. If sulfuric acid be heated with metals or other reducing agents sulfur dioxide is formed. Thus with carbon:  $2\text{H}_2\text{SO}_4 + \text{C} \rightarrow 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{CO}_2$ ; with metals the sulfates are formed as:



or by addition



3. Sulfites treated with concentrated sulfuric acid form the most convenient source of small amounts of the oxide; for example, if concentrated sulfuric acid be dropped into a saturated solution of sodium bisulfite,  $\text{NaHSO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{H}_2\text{O} + \text{SO}_2$ , a steady stream of sulfur dioxide is produced which may be dried by passing it through concentrated sulfuric acid.

Modifications of these methods are employed for, or incidentally result in, the preparation of the oxide, but all are typified by those cited.

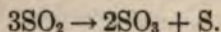
**Properties.** — Sulfur dioxide is a gas at ordinary temperature which has a characteristic odor. It is a blood poison and causes a peculiar and irritating effect upon the throat and lungs. It is injurious to vegetation and its disposal forms an interesting chapter in the development of utilization of by-products. (See the Cottrell Process.) At  $-8^\circ$  the gas condenses to a clear, colorless liquid, and at  $-70^\circ$  changes to a white solid. The gas may, therefore, be readily liquefied by cold and pressure. It is marketed

in glass syphons or steel cylinders or cans. At 20° its pressure is but 3.25 atmospheres, so that the heavy cylinders used for ammonia and carbon dioxide are not necessary. By rapid volatilization of the liquid, temperatures as low as -50° can be easily obtained. It may therefore be, and is, used for purposes of refrigeration.

The liquid is an excellent solvent for sulfur, iodine, phosphorus, rosins and many other substances. The solutions of ionogens in sulfur dioxide are somewhat better conductors than the same substances in water. The reconciliation of the results with the hypothesis of ionization is at present impossible and the reasons for this failure of the theory to square with facts does not yet appear.

The specific gravity of the gas is 2.264 and consequently the weight of a gram molecular volume is 65.54 and the corrected molecular weight 64.06. The critical pressure is 79 atmospheres at a critical temperature of 157°. The solubility of the gas is approximately 50 vol. to one of water, and the solution behaves as an acid, the properties of which are discussed below. Yet on being warmed the gas is liberated and no constant boiling hydrate is formed.

**Chemical Properties.** — The gas, if heated sufficiently to upwards of 1200°, decomposes into sulfur and sulfur trioxide, probably according to the equation,



This action is reminiscent of the behavior of hypochlorous acid (*q. v.*) and it will be seen to be representative of the behavior of its derivatives and is of rather general application (*cf.* sulfites and phosphites).

This reaction may also be effected by sparking with electricity. It also appears to take place under the influence of light. The gas is ordinarily considered as neither combustible nor a supporter of combustion and may be used as a fire extinguisher, yet some substances are capable of burning in it; as, for example, magnesium ribbon, if ignited and plunged into it continues to burn. Iron reacts when heated with the gas to produce iron oxide and sulfide. It also effects the oxidation of hydrogen sulfide, even at room temperature, as in the reaction already given (p. 222). On the contrary, the oxide is capable of acting as a reducing agent, as when with chlorine it unites directly to form sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , the reaction being facilitated by light. Also when sulfur dioxide and oxygen are passed together over finely divided platinum they unite to form  $\text{SO}_3$ . (See contact process for sulfuric acid.) When sulfur

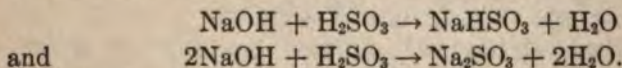


dioxide is formed from oxygen and sulfur, in the solid condition, no change in volume takes place after the initial temperature has been regained. This, as well as the molecular weight, indicates its formula as  $\text{SO}_2$  and in the absence of any evidence to the contrary would indicate a valence for the sulfur of four and a constitutional formula,  $\text{O} = \text{S} = \text{O}$ .

It is perhaps in order to again call attention to the extension of the terms oxidation and reduction. In any case where we have reason to believe that the positive valence of any element or radical is raised or negative valence decreased we use the term oxidation. In any case where the positive valence is decreased or negative valence increased we have reduction. In this sense it will be seen that both terms must always be applicable whenever one of them is, i.e., oxidation of one substance is only possible by simultaneous reduction of another. (See also Electronic hypothesis.)

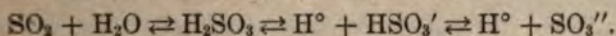
**Sulfurous Acid.**—This term is properly applied only to the solution of sulfur dioxide in water, though sometimes the gas itself is referred to as sulfurous acid, of which it is, properly speaking, but the anhydride. The reaction presumed to take place when sulfur dioxide dissolves in water is indicated by the equation  $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ . In view of the fact that the pure compound has never been isolated, it may be well to indicate the kind of evidence leading to this conclusion.

The solution of the gas is acid in reaction. This might by itself seem conclusive were it not for the fact that when the solution is heated the gas wholly disappears, and the further fact that the solubility at slightly elevated temperatures accords with Henry's law (*q.v.*), which is not ordinarily the case when chemical reaction takes place between a gas, as solute, and the solvent. However, when the solution is treated with bases we get salts which, according to the quantity of base used, are either acid or neutral salts. This behavior would correspond to the reactions:



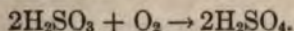
These salts could scarcely be formed were the acid not present. Moreover, the behavior of the acid in all respects conforms to what we should expect from the principles of homogeneous and heterogeneous equilibrium if the reaction were, as indicated above, a readily reversible one. Removal of sulfur dioxide disturbs the system in the direction indicated by the reverse arrow  $\leftarrow$  and of

sulfurous acid by bases or otherwise, in the direction→. We are hence dealing with a system rather than one substance when we consider the behavior of sulfur dioxide in water.

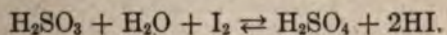


At low temperatures several hydrates have been reported as formed. It appears certain that one at least,  $\text{H}_2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ , really exists.

On allowing the solution to stand in the sunlight it reacts as indicated by the equation  $3\text{H}_2\text{SO}_3 \rightarrow 2\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$ . If the solution stands with free access of air oxidation takes place slowly with formation of sulfuric acid:

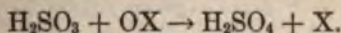


If the solution be treated with chlorine, bromine or iodine, it is also slowly oxidized to sulfuric acid. Thus

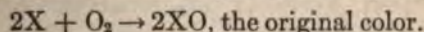


This reaction may be used as a quantitative means of estimating the amount of sulfurous acid in a solution, but the reverse reaction takes place to an appreciable extent if the concentration of the "sulfur dioxide" exceeds 0.05 per cent.

Sulfurous acid is a sufficiently powerful reducing agent to reduce many coloring matters, such as indigo, magenta, etc. It is, therefore, extensively used for bleaching. At all times, it is not apparent that the colors are really *reduced*, since many colored materials are basic and form sulfites of colorless or less highly colored type. In either case exposure to the air, particularly in the sunlight, will reverse the reaction. Thus if we bleach straw, wood pulp, grass or flowers by sulfurous acid or moist sulfur dioxide, if the reaction is a reduction we have:

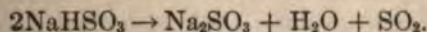


On removal from the solution we get by the exposure to the air:



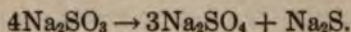
This fairly satisfactorily accounts for the yellowing of paper, straw hats, etc., by exposure.

**Sulfites.**—The acid sulfites on being heated decompose first into neutral sulfites as indicated:





This behavior is characteristic of all acid salts of volatile, or of unstable acids. The neutral salts on being further heated undergo a decomposition analogous to that alluded to on p. 227.



The sulfitcs, like the free acid, are readily oxidized by oxidizing agents to sulfates. The oxidation rate is retarded by sugar or glycerine. These are, therefore, negative catalyzers.

**Uses of Sulfur Dioxide.** — Sulfur dioxide is used as a refrigerant, as a disinfectant and as a reducing agent. In the two first mentioned applications the gas is the active factor, though perhaps a large part of the disinfecting or germicidal activity is due to the change first to sulfurous and then to sulfuric acid, the latter causing the death of the organisms affected. In any case in bleaching fruit both disinfection and sterilization are advantageously produced. Unfortunately, it is not perfectly clear that fruit so treated is as healthful as the unbleached and spore infected varieties and we may have to return from white to brown dried fruits.

For many sorts of disinfection formerly effected by sulfur dioxide formaldehyde is now used, such as disinfection of clothing and houses after contagious disease. In other cases it is supplanted by chlorine. In fact powerful germicides of various sorts are rendering of less importance this once very popular reagent.

On the other hand, as a bleaching agent, particularly in the form of acid sulfitcs, its use is increasing since the texture of the bleached materials is not so seriously affected as in case chlorine is used. Where chlorine must be used, the traces of chlorine left in the fabric bleached and which would be injurious were it to remain are removed by sulfurous acid. It was formerly rather extensively used as a preservative for wines, and other liquors, but this, as well as its use on "hamburger" steak and other meats, is prohibited by the pure food control.

#### SULFUR TRIOXIDE AND SULFURIC ACID

**Occurrence.** — As intimated previously, sulfur trioxide is formed in small amounts when sulfur is burned and both for this reason and because sulfurous acid readily oxidizes on contact with air sulfuric acid is found in small quantities in streams in volcanic regions and in the "pit water" of mines of sulfide ores. The trioxide naturally does not occur in nature. Sulfates are, of course, abundant, as has been already mentioned (*cf.* p. 213).

**History.**—Sulfur trioxide was apparently known under the name of "philosophical salt" to Basil Valentine in the fifteenth century, he having made the same by distillation of calcined vitriol:  $\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$ . It was recognized as the anhydride of sulfuric acid by Guyton de Morveau (a participant in the Nomenclature of Chemistry with Lavoisier, Berthollet and Fourcroy) in 1786.

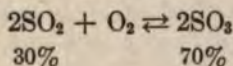
Sulfuric acid, made by distillation of alums (*q.v.*) and vitriols (*q.v.*), was known to the ancients, being mentioned by Geber and others as early as the thirteenth century, and in the fifteenth century it was known to be produced by burning sulfur and niter together and each of the methods was supposed to produce different "spirits." Their identity was recognized by Libavius (1595) and by Boyle (1664) and the manufacture on a commercial scale of a very powerful acid (see pyrosulfuric acid) was carried out by distilling ferrous sulfate, as early as 1755 at Nordhausen. The acid was very expensive and a great step forward was made when Dr. Ward conceived the idea of burning sulfur and niter together in the presence of water under large glass domes and repeating until a very concentrated acid was obtained. This was in 1740. The fuming acid was called Nordhausen or German acid, and that manufactured by Ward, as "Oil of Vitriol by the Bell," or English acid. The latter process was much cheaper, the price being reduced from about \$3.25 to 60 cents per pound. In 1746, lead was substituted for glass vessels, and in 1793, Clement and Desormes showed that the process could be made continuous by using oxides of nitrogen as a catalytic agent. The Gay-Lussac tower was added to the process of manufacture in 1827 and Glover's tower in 1859. In 1831, Phillips, an Englishman, took out patents for the manufacture of the acid by the so-called contact process, but by reason of the difficulties encountered in the process it was not until 1901 that Knietzsch put it into practical effect, and at the present time pure acid is marketed at 9 cents per pound and commercial acid by the chamber process at 1.5 cents. This somewhat statistical résumé is given because sulfuric acid is the most important of all the acids and several million tons represent the annual output and the price of numerous commodities and the cost of almost innumerable manufacturing processes is affected by the price and purity of this substance.

**Preparation.**—1. **The Contact Process.**—If oxygen and sulfur dioxide be heated together only small quantities of the trioxide

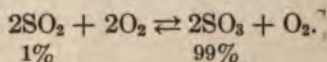


are produced. This is because increase in temperature favors the reverse reaction  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ . Indeed, at  $1000^\circ\text{C}$ . the decomposition of  $\text{SO}_3$  is practically complete and at lower temperatures the direct action is too slow for practical purposes. If, however, the mixed gases interact in the presence of finely divided platinum, which is ordinarily distributed on asbestos fibers, the interaction is rapid and almost quantitative at  $400^\circ\text{C}$ . The explanation of this catalytic process is, according to Ostwald, that the gases are occluded by platinum and the more rapid reaction is due to increased concentration. Whether this is correct or not, it is true that the air and sulfur dioxide used must both be carefully purified or else the catalytic effect of the platinum is destroyed. This "poisoning of catalyzers seems to be caused by many of the same substances which produce toxic effects upon the animal system, where, indeed, the effect may be the same, *i.e.*, the inhibition of the activity of the animal enzymes, or catalyzers, which maintain the body equilibrium." At any rate, the "poisoning" effect of arsenic on platinum is very marked and the presence of traces of this substance in sulfur and other sources of sulfur dioxide was the chief cause of the long interval between the discovery and the successful practice of the method. (On so small a factor sometimes hinges success or failure.)

Many other catalyzers, such as ferric oxide, chromic oxide, pumice stone, etc., may be used, but since catalyzers do not affect the point of equilibrium, but only the speed at which it is established, a catalyzer must effect a rapidity of action, in such a case as this, sufficiently great to be practical at a temperature where the equilibrium is at the desired point. Ferric oxide works sufficiently rapidly at  $625^\circ$ , but at this temperature the reaction is in equilibrium when



and consequently 30% of the dioxide goes over unchanged. With platinized asbestos, on the other hand, at  $400^\circ$  its point of equilibrium with twice the proportion of oxygen needed is



This advantage of the use of platinized asbestos more than offsets

its greater cost. The heat of reaction is 22,730 cal. and more than maintains the needed temperature of the apparatus.

When sulfur trioxide is dissolved in water sulfuric acid is formed and, since the raw materials,  $\text{SO}_2$  and air, must be carefully purified, the acid so produced is practically pure. All the c. p. acid now on the market is prepared in this manner. An outline drawing illustrating the process is presented by Fig. 64.

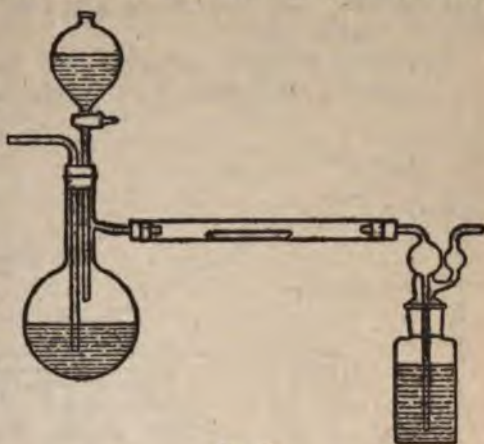


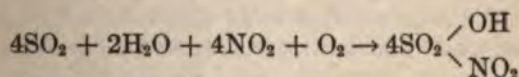
FIG. 64.

## 2. The Chamber Process.

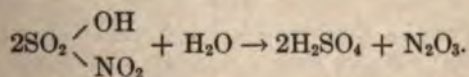
— If sulfur dioxide and air are allowed to come into contact in the presence of water and of nitric acid or of oxides of nitrogen sulfuric acid is produced. In order to effect this

reaction most economically all factors are made to interact in the gaseous condition. The liquid is in relatively small bulk and, consequently, to secure a large output very large lead chambers are employed, sometimes of a capacity approximating 200,000 cu. ft.

The chemistry of the reactions which take place in these chambers is somewhat uncertain, but is usually assumed to be as follows:



The compound formed is known as nitrosyl sulfuric acid. If the amount of steam used in the reaction is limited this substance is sublimed on the walls of the chambers. With water nitrosyl sulfuric acid reacts to produce sulfuric acid and nitrous anhydride (*q.v.*).



The nitrous anhydride with oxygen of the air forms nitrogen



peroxide,  $\text{NO}_2$ , by direct action,  $2\text{N}_2\text{O}_3 + \text{O}_2 \rightarrow 4\text{NO}_2$  and is hence ready to react again with water and sulfur dioxide and oxygen. The oxide of nitrogen is, then, a catalytic agent and may be considered to operate by substituting two rapid reactions for a slow one, *i.e.*, the two above given for the oxidation of  $\text{H}_2\text{SO}_3$  by air. (See p. 229.)

Since the nitrogen peroxide may be used again and again, the process is cheapened if its escape is prevented. An outline

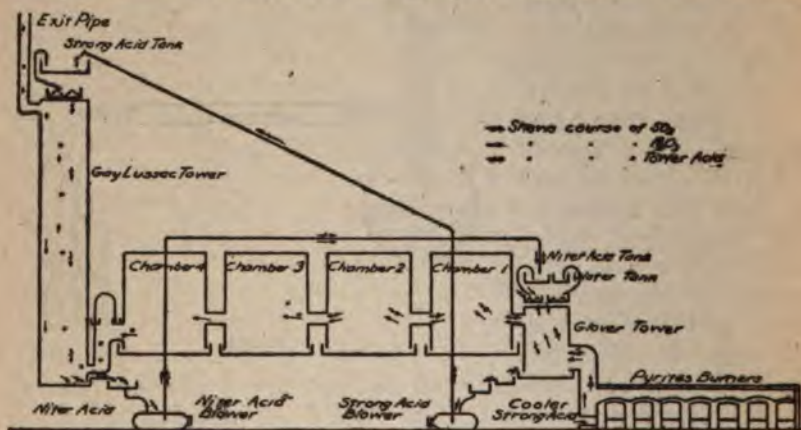
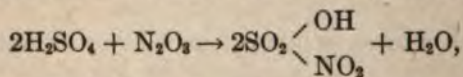


FIG. 65.

drawing will indicate how this is effected. (See Fig. 65.) The incoming gases as they react condense and settle in the bottom of the chambers so far as the sulfuric acid and water are concerned, but the inert gases sweep the oxides of nitrogen eventually through the Gay-Lussac tower, which is filled with tiles, or other refractory material, over which concentrated sulfuric acid trickles. Here

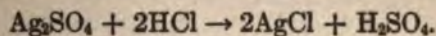


which dissolves in sulfuric acid and is pumped to the top of the Glover tower, where it is allowed to trickle down a similar tile structure, while being diluted with water. The reaction in the Gay-Lussac tower is thus reversed and since the stream of sulfur dioxide from the burners enters through this tower the oxides of nitrogen are mechanically swept into the chamber to repeat their chemical gymnastics. In the meantime the hot gases reconcentrate

the acid so that by the time it reaches the bottom it is again ready to be pumped to the top of the Gay-Lussac tower.

The process is worthy of more detailed study, not only because of its importance, but because its study reveals the minutiae necessarily involved in the practical, economical operation of a chemical industry. (See Thorpe's Industrial Chemistry.) The acid which collects at the bottom of the chambers must be kept at a concentration of not more than 70% by excess steam else the walls of the chambers would be attacked. It is also very impure by reason of the materials which accompany the ingress of the air, water, sulfur dioxide, and oxides of nitrogen. The excess water is driven off by evaporation in cast iron pans, but the impurities may only be separated by distillation. For many purposes this impure acid is wholly suitable and large quantities are so used. Before the success of the contact process, the pure acid was prepared by distillation in retorts made of gold lined platinum, which, of course, is expensive, and the high temperature required added to the expense.

3. **Other Methods.** — Sulfur trioxide may be made by distillation of anhydrous sulfates as has already been indicated, and the acid, more or less dilute, by distillation of the hydrated sulfates (*q.v.*). The trioxide may be obtained from the acid by distillation with a non-volatile acid oxide, capable of forming a more stable acid. The only available one is phosphorus pentoxide, the reaction being as indicated:  $\text{P}_2\text{O}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HPO}_3 + \text{SO}_3$ . Also the acid may be prepared by distillation of the salts with a less volatile acid, as  $\text{Na}_2\text{SO}_4 + 2\text{HPO}_3 \rightarrow 2\text{NaPO}_3 + \text{H}_2\text{SO}_4$ . A consideration of the paragraph on p. 198 indicates that sulfuric acid might also be prepared by treatment of a soluble sulfate with any acid with which the metal will form an insoluble salt. This method is frequently employed, rather unconsciously, in the precipitations involved in quantitative and qualitative analysis, *e.g.*,

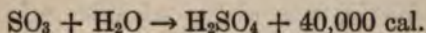


**Physical Properties of Sulfur Trioxide.** — Sulfur trioxide exists in two allotropic modifications, one known as a sulfur trioxide, has a boiling point of 46.2° and, if cooled to 16°, it crystallizes in long needles, melting at 14.8°. Its vapor has a density of 2.76, which corresponds to a molecular weight of 80 expressed by the formula  $\text{SO}_3$ . If it be kept at 16° for some time it passes



over into an asbestos-like mass, melting at 25°. At higher temperatures this so-called  $\beta$  variety goes over to the  $\alpha$  form. Its molecular weight in solution in phosphorus oxychloride is approximately 160, so that the two forms are probably expressed by the formulas  $\text{SO}_3$  and  $\text{S}_2\text{O}_6$ .

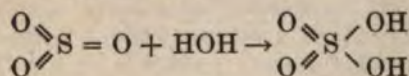
**Chemical Properties.**—The oxide dissociates rather readily into sulfur dioxide and oxygen at elevated temperatures, the dissociation being practically complete at 1000°. Sulfur trioxide unites with many metallic oxides directly to form sulfates, *e.g.*,  $\text{Na}_2\text{O} + \text{SO}_3 \rightarrow \text{Na}_2\text{SO}_4$ . (See Berzelius' dualistic hypothesis.) With water it reacts with the evolution of much heat to form sulfuric acid:



As is to be expected from its decomposition by heat, sulfur trioxide is a ready oxidizing agent, but is seldom used for the purpose. Its chief characteristic is its avidity for water, which it is able to abstract from such substances as starch, sugar, wood-fiber, etc. This ready union with water is also the occasion for the fumes which are formed when it is exposed to the air or formed through decomposition by heat of sulfuric acid or sulfates. (Cf.

p. 125.) We may formulate graphically the oxide as  $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} = \text{O} \\ \parallel \\ \text{O} \end{array}$  and

without doing violence to any facts assume that the union with water takes place as indicated:

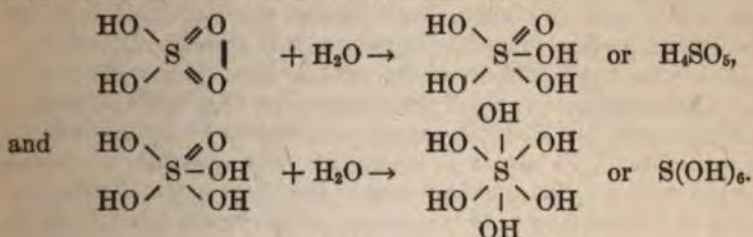


If this be the correct formulation, we may then regard the sulfate in both oxide and acid as hexavalent.

**Physical Properties of Sulfuric Acid.**—Sulfuric acid is an oily liquid, "oil of vitriol," with a specific gravity of 1.85. It melts at 10°. The pure acid boils at 270° with partial decomposition until a concentration of 98 per cent is reached, *i.e.*, the  $\text{SO}_3$  escapes, while the water remains behind. The solution distills over unchanged at 317°. This is the liquid commonly known as concentrated sulfuric acid with a specific gravity of 1.84.

**Chemical Properties of Sulfuric Acid.**—The acid is rather readily decomposed by heat into water and sulfur trioxide and this dissociation is practically complete at  $450^{\circ}$ . It is perhaps desirable to describe the chemical behavior of the acid under three heads, its action as a dehydrating agent, as an oxidizing agent and as an acid.

1. Concentrated sulfuric acid when mixed with water evolves heat and the volume of the resulting mixture is less than the sum of the constituents. (See lecture experiments.) These indications of chemical change may perhaps be accounted for on the assumption of a union with the water, analogous with that which takes place in the formation of sulfuric acid itself. Thus

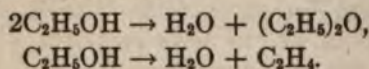


This would account for three acids,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_4\text{SO}_5$ ,  $\text{H}_6\text{SO}_6$ . A fourth is discussed under the term *pyrosulfuric acid*. The partial substantiation of this view we have in the fact that when concentrated solutions of sulfuric acid are strongly cooled, there is formation of crystals having the composition represented by the formula  $\text{H}_2\text{SO}_5$ , which melt at  $8^{\circ}$ . Unfortunately the corresponding hydrate with two molecules of water has not been definitely isolated. Moreover, the evolution of heat with addition of water continues even after water to the proportion of  $2\text{H}_2\text{O} \cdot \text{H}_2\text{SO}_4$  has been added. The maximum heat of dilution, *i.e.*, when one gram molecule of acid is added to an indefinitely large volume of water (infinite dilution) is approximately 19,400 cal. It is at present impossible to say how much of this heat of solution is due to the formation of hydrates (see below) and how much to ionization of the acid and to the process of "solution" as the term is ordinarily used. In any case, the application of the phase rule (*q.v.*) indicates the existence of a hydrate,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , melting at  $-25^{\circ}$ , and furnishes some evidence for the existence of the normal acid  $\text{S}(\text{OH})_6$ , or  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , which is supposed to exist and to melt at  $-70^{\circ}$ . (See Chap. XIII.)

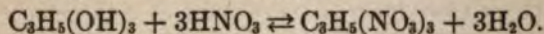
Three practical results follow from this behavior of sulfuric acid



with water. The heat of dilution is so great that breakage of glass vessels and spattering, with unpleasant consequences, are likely to occur if the two are carelessly mixed. The mixing should *always* be effected by pouring the acid into water, so that it may immediately sink beneath the surface; the water should also be stirred to distribute the heat and prevent cracking of the vessel, if of glass. A second consequence is that, since the vapor tension of strong acid solutions is very low, water vapor present in air or other gases is readily absorbed and hence the acid is frequently used for drying purposes, both by passage of the materials to be dried through it, or by allowing them to stand in closed vessels in the presence of it. In this latter case, of course, the vapor in the vessels is replaced by the substance being dried as rapidly as it is absorbed by the acid so long as the vapor tension of the substance is greater than that of the acid solution. A third consequence is that sulfuric acid is frequently used to absorb the water, or elements to form water, in reactions where such action is desirable. For example, if alcohol is treated with sulfuric acid and heated the effect is the withdrawal of water and, according to the temperature employed, ether,  $C_4H_{10}O$ , or ethylene,  $C_2H_4$ , are produced:

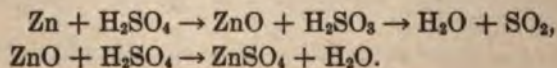


Again in reversible reactions where water is one of the products, its effect is nullified by union with the acid. This is illustrated by its use in the preparation of nitroglycerine:



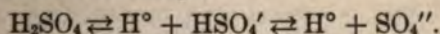
If concentrated sulfuric acid is present the withdrawal of the water by it allows the process to go to practical completion in the direction  $\rightarrow$ .

2. Sulfuric acid, like its anhydride, is a powerful oxidizing agent. This has already been illustrated by its behavior in the preparation of sulfurous acid and its anhydride. Most of the reactions in which the concentrated acid is used are in fact of this type. Practically all metals, except gold, platinum, iridium and rhodium, and most non-metals are so oxidized. This action may be again mentioned in connection with zinc. The oxides of the metals first produced are usually dissolved, due to the acid character of the substance. Thus:



Some confusion, of course, arises from the fact that hot sulfuric acid is readily reduced by hydrogen, so that in the case of the metals above hydrogen in the electromotive series (*q.v.*) it may be that hydrogen is first produced. There would seem to be little reason for assuming this to be true, as do some authors, at least in the case of copper, arsenic, etc., which with other acids and with dilute sulfuric acid fail to liberate hydrogen. Indeed, the ionization of concentrated sulfuric acid is so slight that its oxidizing effect is that which ought to be expected.

3. When sulfuric acid is diluted with water it shows a chemical behavior typical of acids and indeed of a character intermediate between the very active acids, nitric, hydrochloric and permanganic, and the weaker acids, such as acetic. In this relation it behaves as a dibasic acid and furnishes two series of salts, the acid and neutral salts. The acid salts are more readily formed the stronger the acid, and this, as well as the degree of ionization, and the behavior during electrolysis (see persulfuric acid) indicates that ionization takes place in two steps:



Indeed, the evidence seems to show that the second step takes place appreciably only after the first has reached a degree of dissociation equal to 50 per cent, which in the case of sulfuric acid is about a normal solution, as indicated on p. 175. Sulfuric acid solutions stronger than normal are, therefore, to be regarded as essentially monobasic.

The extensive use of the acid as an acid is partially due to its comparatively large ionization at moderate dilutions, but more to its non-volatility, which enables the chemist not only to liberate other acids from their salts by its use, but to drive the reactions to completion by volatilizing them. This has already been abundantly illustrated. (*Cf.* p. 148.) The value of the acid for such operations is somewhat decreased by its oxidizing power, illustrated by the cases of hydrobromic and hydriodic acids (*q.v.*).

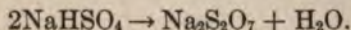
**Uses.** — The uses of sulfuric acid are not only numerous, but in many cases are on an enormous scale; as in the preparation of other acids from their salts, in the manufacture of phosphate fertilizers (*q.v.*), in the manufacture of guncotton and nitroglycerine, sodium sulfate for soda and glass manufacture, in purification of petroleum and other oils, in the manufacture of dyes, in many



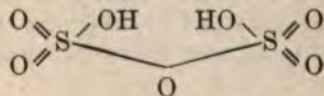
electrolytic processes, as copper refining, etc. One of the most interesting cases is the use of sulfuric acid in the manufacture of storage batteries, which are extensively used by electric lighting and other companies to carry their "peak load." Another specially interesting application on a large scale is as a cleansing agent for sheet iron before dipping, in the manufacture of tin plate. Minor, though still extensive, uses are in the separation of silver from gold in refining the latter, in the preparation of hydrogen and the manufacture of sulfates which have commercial application, etc. Its uses in small quantities in chemical and other operations are entirely too numerous to mention.

**Sulfates.** — The sulfates which are of importance are very numerous and will be discussed separately with the metals which are a part of each. Many are minerals found in large quantities; others are manufactured, some on a very large scale.

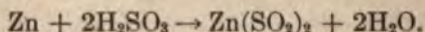
**Other Acids and Oxides of Sulfur.** **Pyrosulfuric acid.** — When sulfur trioxide is passed into concentrated sulfuric acid it dissolves, forming a liquid which fumes continuously on exposure to the air. This was the Nordhausen acid previously mentioned as made by distillation of sulfates. Its sodium salt may also be made by heating sodium acid sulfate, hence the name pyro (from  $\pi\rho$  = fire), which is prefixed to the name of many substances obtained similarly.



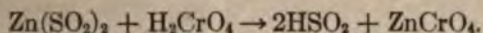
If the quantity of sulfur trioxide exceeds 40 per cent the mass is solid at ordinary temperature and is sold under the name solid sulfuric acid. If the acid is dissolved in water ordinary sulfuric acid is, of course, produced. It may be regarded, then, as a hydrate of sulfur trioxide  $2\text{SO}_3 \cdot \text{H}_2\text{O}$  and perhaps has the graphic formula:



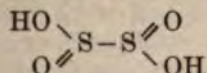
**Hyposulfurous Acid.** — If zinc, or other metals, be treated with sulfurous acid, they slowly dissolve, but no hydrogen is evolved, and the solution contains the salt of an acid which has the empirical formula  $\text{HSO}_2$ .



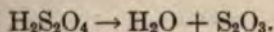
The salts may also be obtained in other ways; as, for example, by treating zinc with a solution of sulfur dioxide in absolute alcohol. The acid may be liberated by treating the salt with an acid capable of forming an insoluble salt with the metals as, for example, with chromic acid.



The acid is known only in aqueous solution and its composition is inferred from the depression of the freezing point produced by the sodium salt. It is probably  $\text{H}_2\text{S}_2\text{O}_4$  and the graphic formula is

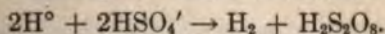


The sodium salt of the acid is extensively used in the dyeing industry, since it is an exceptionally powerful reducing agent. Could it be dehydrated, the acid would give as its anhydride, sulfur "sesquioxide." \*



The oxide may not be obtained in this manner, but is supposed to be obtained when sulfur is dissolved in Nordhausen acid or when sulfur and sulfur trioxide are brought into direct contact. It makes a green crystalline mass as a solid, and a blue solution in sulfuric acid. (These colors are extraordinary if the substance is as supposed.)

**Persulfuric Acid.**—If a 50% solution of sulfuric acid, kept at zero by a cooling bath, is electrolyzed with not too strong a current, oxygen is liberated at the anode in very small quantity and the solution around the anode is materially changed in character. The reaction which takes place may be indicated:

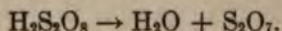


This latter acid is known as persulfuric acid and its potassium or ammonium salt is readily obtained, by electrolysis of concentrated solutions of the corresponding acid sulfates, in crystalline masses about the anode. These salts are coming into use rather extensively at present, since they are powerful oxidizing agents. They were first prepared in 1891 by Marshall. The free acid is

\* The term "sesqui" is a relic from an older nomenclature and refers to the fact that the relation of the elements in atomic proportions is 1 : 1½. We still encounter the term occasionally.



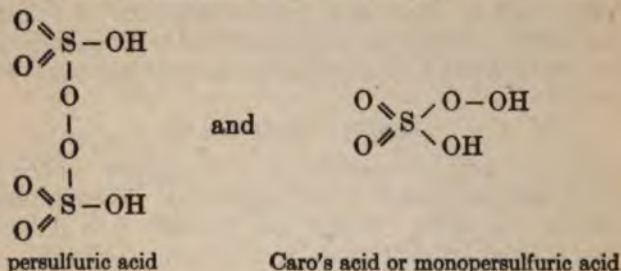
quite unstable. If its anhydride were obtained by elimination of water it should be



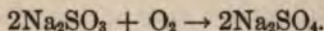
This substance may be obtained, by sparking a mixture of sulfur dioxide and oxygen, in the form of oily drops, which form at  $0^\circ$  a white solid. In solution in water it forms the persulfuric acid.

If hydrogen peroxide be added to sulfuric acid an acid which has the composition represented by  $\text{H}_2\text{SO}_5$  is obtained, known as Caro's acid, from its discoverer (1898).

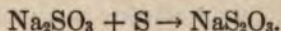
Both these acids have properties relating them to hydrogen peroxide and for reasons which are perhaps not essential at this point are assigned graphic formulas as follows:



**Thiosulfuric Acid and the Polythionates.**—When we consider that sulfur is the second member of the oxygen group, it is not surprising to find that in certain cases sulfur may be made to perform a function similar to that of oxygen. If sodium sulfate in solution,  $\text{Na}_2\text{SO}_3$ , is exposed to the air, it gradually absorbs oxygen, forming the sulfate



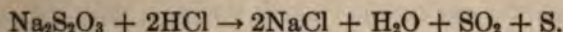
In a similar manner, if it be allowed to stand with flowers of sulfur, the same sort of reaction takes place (hastened by gentle warming; sometimes called "digestion").



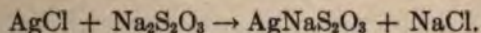
The name thiosulfuric is derived from the Greek word *θειων* = sulfur, and is considered more euphonious than would be sulfo-sulfuric.

The salts of this acid are also capable of being prepared in many other ways. One of the salts has found extensive use in photography as a solvent of silver chloride and other silver salts,

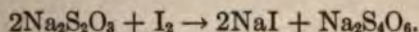
from photographic plates and hence is a familiar substance. This is the hydrate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and is known as "hypo," since it was at first supposed to be a salt of hyposulfurous acid. The free acid may not be prepared, since it breaks down at once into water, sulfur dioxide and free sulfur:



The reaction so useful to the photographer may be expressed:



Both salts being soluble, unchanged silver salts may be dissolved out of the developed plates. (See photography.) Thiosulfate also finds application in bleaching operations as an "antichlor" and as a reducing agent. In laboratories it finds its most extensive use because of its behavior with iodine solutions, which are decolorized by it, according to the following reaction:



The latter salt is known as sodium tetrathionate and is a representative of a series of compounds containing sulfur and closely related to sulfuric acid. We will content ourselves here with giving their formulæ and names, and the student is referred to larger works for details.

Dithionic acid,  $\text{H}_2\text{S}_2\text{O}_6$ .

Trithionic acid,  $\text{H}_2\text{S}_3\text{O}_6$ .

Tetrathionic acid,  $\text{H}_2\text{S}_4\text{O}_6$ .

Pentathionic acid,  $\text{H}_2\text{S}_5\text{O}_6$ .

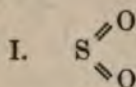
Hexathionic acid,  $\text{H}_2\text{S}_6\text{O}_6$ .

The possibility of the existence of these acids is presumed to be due to the facility with which "chains" of sulfur atoms form by union with each other in a manner similar to that which we shall encounter in a consideration of carbon compounds.

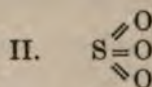
***Constitution of Sulfur Compounds.*** — In order to show more clearly the relationship between the constituents of a compound than is possible by even molecular formulæ the method of expression variously known as constitutional, structural or graphic formulæ has been devised. We have already encountered this in the chap-



ter on the oxygen compounds of the halogens and find it especially advantageous here. It needs to be emphasized, however, that when we propose a graphic formula it is simply to indicate some relationship of the elements which is shown by the behavior of the compounds and is strictly a "graph" and does *not* indicate any space relation and, though perhaps needless to say, does not indicate in any way how the elements in a compound are held together. Thus when we say that the oxides of sulfur have the following structural formulæ:



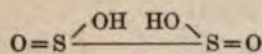
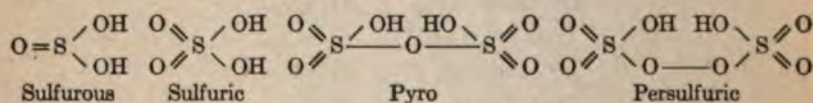
sulfur dioxide



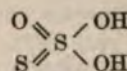
sulfur trioxide

all we mean to convey is that in I, the sulfur is tetravalent and that whatever the character of union between oxygen and sulfur may be, both atoms bear the same relation, and that so far as we know the molecular weight is as indicated. In II the valency of the sulfur is six. It will be noted that structural formulæ are largely imaginary. We shall find them highly useful, provided they are "bounded by coherent reason," and not used without close restriction.

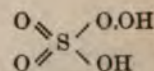
To the acids have been assigned the following structures, some of which have already been given:



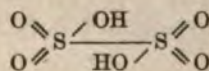
Hyposulfurous



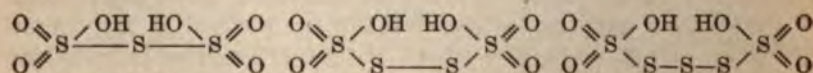
Thiosulfuric



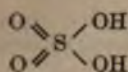
Monopersulfuric



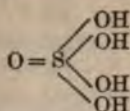
Dithionic



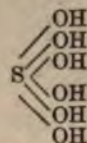
There are also the hydrates of sulfuric acid:



Sulfuric  
I



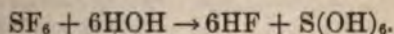
Monohydrate  
II



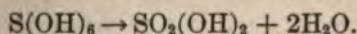
Dihydrate or normal acid  
III

We will content ourselves here by giving a portion of the reasons for the assumption of the formulæ of the last three mentioned. If sulfuric anhydride has the structure indicated, then the simplest reaction between it and water,  $\text{H}-\text{OH}$ , would be expressed by formula I. This would mean that two of the four oxygen atoms would be different from the others. That such is the case is shown by the fact that if phosphorus pentachloride is added to sulfuric acid, the reaction indicated takes place,  $\text{SO}_2(\text{OH})_2 + \text{PCl}_5 \rightarrow \text{P}(\text{OH})_2\text{Cl}_3 + \text{SO}_2\text{Cl}_2$ .

Again, the compound sulfur hexafluoride can be made and by hydrolysis can give sulfuric acid. The most reasonable course for this reaction is



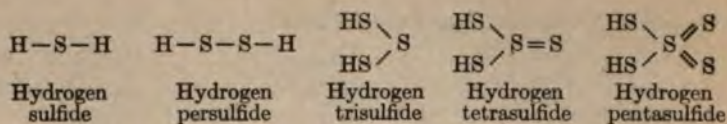
The normal acid solution is unstable and breaks down into



All oxygen acids, like sulfuric acid, contain the so-called hydroxyl group and the essential difference between bases and oxygen acids is that while both invariably possess the hydroxyl (OH) group, bases separate it as an ion in water solution, while acids split off the hydrogen (H) ion. Why this difference, is an unsolved problem, but it appears certain that we have compounds capable of doing both things at the same time. (See amphoteric compounds.) That the formulæ II and III, above, exist in aqueous solution seems reasonable in spite of the fact that definite neutral salts are not prepared, since polybasic acids ionize in steps and the third and fourth ions, and especially the fifth and sixth, are formed only with great difficulty, as would be expected from the principle of mass action. (See also phosphoric acids.)

In a similar manner the sulfides and polysulfides may be assigned the following formulæ:





the last three being certainly known only as salts.

**Selenium and Tellurium and their Compounds.**—These two elements are not widely distributed nor of large occurrence in nature. The selenium compounds are usually associated with sulfur ores and selenium is sometimes found in crystalline form associated with free sulfur. Tellurium is quite rare and is usually found associated with sulfides containing lead, bismuth, silver and gold. Gold telluride is found in some quantity in Colorado, hence the name of the mining town Telluride.

Tellurium was first discovered by Müller Von Reichenstein in 1783 and named by Klaproth in 1788 because of the earthy character of the ores from which it was obtained (from *tellus* = the earth). When, in 1817, Berzelius isolated from the flue dust of the pyrites burners an element of similar properties he named it selenium (from *selene* = the moon). (The imagery is more complete if we recall that sulfur is the element characteristic of Dante's Hell.) The elements are both solid, but selenium volatilizes readily and burns with a blue flame. Tellurium burns, but with more difficulty. Both elements appear to exist in several allotropic forms. In the ordinary form selenium is a reddish brown powder and tellurium a gray metal-like substance.

Neither element is produced in large quantities, partly by reason of the scarcity and partly because they and their compounds in general perform the same functions, though less rapidly, as sulfur. Selenium is peculiarly affected by light with respect to electrical conductivity and is, therefore, used in a number of interesting electrical devices. It is also used to some extent in producing particular tints in glass and enamels and to decolorize ordinary glass. (See glass.) Tellurium is produced in considerable quantities as a by-product in the refining of copper, but has almost no practical uses as yet. It is said to be effective as an aid to isolation of nervous patients since the organic compounds produced by its internal administration are of such intensely unpleasant odor as to make both patient and friends acquiesce in the arrangement. No attempt will here be made to detail the properties of the compounds and their methods of preparation, but the following table

will reveal the relations and the student is referred to larger books for further details.

### The Sulfur Sub-group

	Sulfur.	Selenium.	Tellurium.
Atomic weight.....	32.06	79.2	127.5
Molecular formula.....	$S_8$ - $S_2$	$Se_8$ - $Se_2$	$Te_8$
Melting point.....	114-119°	170-217°	454°
Boiling point.....	448.5°	688°	1390°
Specific gravity.....	1.95-2.06	4.28-4.80	5.93-6.4
Color.....	Yellow	Reddish brown to black	Metallic to black
Formula of hydrogen compound...	$H_2S$	$H_2Se$	$H_2Te$
Boiling point of hydrogen compound.....	-62°	-42°	0°
Specific gravity of hydrogen compound (liquid).....	1.17	2.87	4.48
Dissociation temperature of hydrogen compound.....	400°	150°	0°
Formula of lower oxide.....	$SO_2$	$SeO_2$	$TeO_2$
State of lower oxide at room temperature.....	Gas	Solid	Solid
Formula of higher oxide.....	$SO_3$	$(SeO_3)$	$TeO_3$
Formula of "ic" acid.....	$H_2SO_4$	$H_2SeO_4$	$H_2TeO_4$ ( $H_6TeO_6$ )

This series of elements furnishes a very striking and comprehensive "family group," and it is well worth study not only because of the similarities to be expected in the light of the periodic law, but because the variations are also interesting. An elementary text-book is not the place for such a study, however.

**Exercises.**—1. Why is the sulfur obtained from Louisiana purer than that mined in Sicily?

2. What substances other than sulfur sublime when heated?

3. When molten sulfur is cooled its freezing point varies from 119° to 114° according to the temperature to which it has been heated and the rate of cooling. Why?

4. A given weight of sulfur occupies 100 cc. at 0° C. Its specific gravity is 2.04. What volume will it occupy at the same temperature if completely converted to the monoclinic variety?

5. A measurement of the specific gravity of sulfur vapor gives the value 6.6. On the assumption that it is a mixture of  $S_8$  and  $S_2$ , calculate the percentage amounts of each.

6. 100 grams of silver when heated with sulfur give 114.85



grams of silver sulfide. Calculate the exact atomic weight of sulfur from these values.

7. What effect would an increase of temperature have on the rate of union of hydrogen and sulfur? The dissociation of hydrogen sulfide by heat begins to be appreciable at  $310^{\circ}\text{C}$ . What effect is produced on the equilibrium point by heating to  $500^{\circ}\text{C}$ ? How is the time required to reach equilibrium affected?

8. How is silver affected by hydrogen sulfide? Why is this evidence of the presence of free sulfur and how is the condition of the gas affected by the union of sulfur with silver? Why not ascribe the action to the acid character of hydrogen sulfide?

9. How would you undertake to demonstrate that sulfur dioxide has the formula  $\text{SO}_2$  rather than  $\text{S}_2\text{O}_4$ ?

10. If at  $700^{\circ}$  sulfur trioxide is decomposed to the extent of 40 per cent, what is the specific gravity of the mixture?

11. Sulfur dioxide and chlorine, if brought in contact, unite to form a chloride; what is its composition and what is its reaction with water?

12. On p. 227 it is stated that at  $1200^{\circ}$  sulfur dioxide is partially converted to sulfur trioxide, and on p. 232 that sulfur trioxide is completely decomposed at  $1000^{\circ}$ . Can both the statements be true? How would you undertake to determine if a mixture of the gases exists at a given temperature?

13. If sulfur dioxide and oxygen are heated together in a closed tube at  $400^{\circ}$ , what is the condition when equilibrium is attained? Why is platinum used in the contact process?

14. If nitrogen peroxide is assumed to be added directly to the chambers in the sulfuric acid factories and is produced by the following reactions:  $2\text{KNO}_3 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HNO}_3 + \text{K}_2\text{SO}_4$  and  $2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + \text{O}$ , how many times does it react with sulfur dioxide, before final loss, if 4 kilograms of nitrate are used for every 100 kilograms of sulfur?

15. Make a list of all chemical reactions which you have performed in the laboratory in which sulfuric acid is used and classify them as oxidizing, dehydrating or acid activities of sulfuric acid.

16. Review all the reactions discussed in this chapter and give the volume relations of all gases involved.

## CHAPTER XIII

### THE PHASE RULE

In the preceding discussions we have been somewhat hampered in efforts for clear presentation by lack of certain ideas which were presented by Willard Gibbs (of Yale) in 1876-78. These ideas are formulated under the term "The Phase Rule," which is a special form of the general principle of equilibrium. Before stating the law or rule it is essential that certain terms used be specifically defined. These are system, phase, degrees of freedom and components.

A **system** is any substance or group of substances considered as isolated from any substance or condition by which it may be affected. For example, if we have water in a closed glass vessel we may have only water and water vapor, or we may have ice, water and vapor or ice and vapor. This is a system.

If we now by any means change the proportion of liquid or vapor or ice with respect to each other we say we convert them from one phase to another, *i.e.*, ice may be changed from the solid phase to the liquid phase and this to the vapor phase. The ice is supposed to be homogeneous, as also the liquid and vapor. A **phase** may, therefore, be defined as one of the homogeneous portions of a system.

We have three means, and three only, of disturbing a system in equilibrium, *viz.*, by change of temperature, change of pressure and change of composition. If a system is such that neither pressure, temperature nor composition can be changed without destruction of a phase we have no degrees of freedom.

If we can change the temperature or the composition or pressure without destroying a phase we have one degree of freedom, and if we can change the temperature and, independently, either of the other variables we have two degrees of freedom, etc. Since in a system there may be two immiscible liquids containing substances in solution the composition of which may vary, we may have more than three degrees of freedom. The **number of**



degrees of freedom of a system are then the number of independent variations of temperature, composition, or pressure which can be produced without changing the number of phases of a system.

In a system such as water and water vapor we have one chemical substance, the molecules of water. This is spoken of as a system consisting of two phases but of one component. A **component**, is, then, a chemical individual which takes independent part in a change of equilibrium, but is not decomposed in the process. This statement is a little unclear, but perhaps we may proceed to the statement of the law and give enough illustration to make its meaning and utility clear. Willard Gibbs reached the conclusion that when a system is in equilibrium the number of phases, plus the number of degrees of freedom, equals the number of components plus two, or  $P + F = C + 2$ , where  $P$  = phases,  $F$  = degrees of freedom and  $C$  = components.

The phase rule serves two purposes: as a basis for the classification of similar systems of equilibrium and as a means of determination of the number of components where phases and degrees of freedom are known.

**Non-Variant Systems.**—If a system has no degrees of freedom it is said to be non-variant. An illustration is furnished by ice, water and water vapor in equilibrium. If we have such a system in equilibrium enclosed in a cylinder with a movable piston we find the pressure of water vapor on the piston equal to 4 mm. of mercury, the vapor tension of water at 0°. If we attempt to increase the pressure by adding weights to the piston instead of causing increase of pressure by concentration of vapor, the vapor condenses to water. If we attempt to heat the system no change in composition of ice or water or water vapor occurs. The ice simply melts. If we attempt to increase the concentration of water vapor by introducing more of it, it simply condenses, *i.e.*, we can change the equilibrium of water, ice and water vapor neither by change of temperature, composition nor pressure so long as all three phases exist. The system is non-variant, so long as we have one component, water, and three phases

$$P + F = C + 2, \text{ or } 3 + 0 = 1 + 2.$$

This condition obtains for all systems where the number of phases exceeds the number of components by two.

**Univariant Systems.** — If to the above system we supply heat until the ice is converted to water continued heating raises the temperature and simultaneously the vapor pressure is increased. According to the phase rule this system is univariant since we have two phases, water vapor, and one component, *i.e.*,  $2 + F = 1 + 2$  and therefore  $F = 1$ . We may at will change one of the variables without destroying a phase but the other variables must alter correspondingly.

The system, ice and water, is likewise univariant. Ice and water are in equilibrium at  $0^{\circ}$ . If pressure is applied to the system ice melts, since the volume of water is less than of ice and according to Le Chatelier's theorem the change to water will tend to lessen the pressure. In changing from ice to water heat is absorbed and hence the temperature of the system falls. Fixing the pressure on any ice-water system therefore determines the temperature of equilibrium. Experiment shows that the melting point of ice is lowered  $0.0075^{\circ}$  for each atmosphere of pressure.

**Bivariant Systems.** — When we heat water at a constant pressure, *e.g.*, at atmospheric pressure, until the vapor pressure is equal to the pressure applied, then so long as heat is supplied no state of equilibrium can be reached, for so long as the pressure is fixed the temperature must likewise remain fixed. When all the water in the system is converted into steam we have a system consisting of one phase and one component. It should, by the phase rule, be bivariant and consequently have two independent variables. This is the case, as is shown by the fact that both pressure and temperature may be changed without change of phase.

**Polyvariant Systems.** — Only one example of a system having more than two degrees of freedom will be given. A trivariant system is illustrated by a salt solution. Here we have but one phase, liquid and two components, solute and solvent,  $1 + F = 2 + 2$ , and therefore  $F = 3$ . We have three independent variables and hence even when pressure and temperature are held constant we can vary the composition of the solution between wide limits. The facts are in accord with the phase rule. If, however, we have two phases, *e.g.*, a solid and liquid, the system becomes divariant and fixing the temperature and pressure fixes also the composition. This accords with fixed solubility at a given temperature and pres-



sure. If all water be chemically combined with the solute we have a non-variant system since we have but one component.

**Graphic Illustration.**—A convenient method of presenting the relations which have just been discussed is illustrated by figures 66 and 67. Fig. 66 shows the conditions of equilibrium for the various systems of water, ice and water vapor. Ice, water and vapor can exist in equilibrium only at one temperature and pressure, the triple point. The other systems may exist as indicated by the lines in the diagram. It will be observed that a non-variant system is represented by a point, a univariant system by a line, and a divariant system by an area. Trivariant and higher systems require a greater number of coördinates and their discussion would lead us beyond our present purpose.

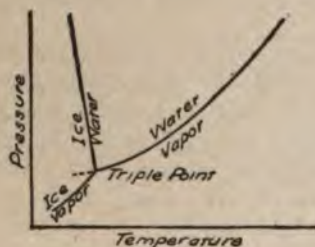


FIG. 66.

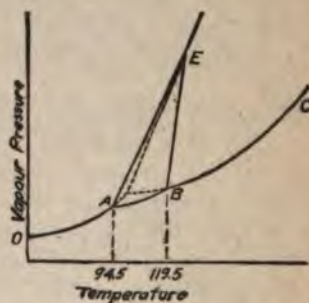


FIG. 67.

Figure 67 presents a similar diagram for sulfur systems. In this figure the line *OA* represents the variations of temperature and pressure for equilibrium between rhombic sulfur and sulfur vapor; *AB*, monoclinic sulfur and vapor; *BC*, liquid sulfur and vapor. The line *BE*, the conditions for equilibrium between monoclinic sulfur and liquid. It may be specially noted that the line *AE* represents the melting point of rhombic sulfur and slopes to the right, since the volume of liquid sulfur is greater than that of solid sulfur. This effect of pressure accords with Le Chatelier's theorem.

**Metastable Equilibrium.**—Ordinarily when we have a system in equilibrium and change the conditions so that a change of phase should occur, the change takes place at once. Suppose, for example, we have a saturated solution of a salt in equilibrium

with the solid solute and the temperature is reduced. If the solute is less soluble at lower temperature some salt crystallizes out. This is the ordinary behavior. There are cases, however, in which, for reasons yet undetermined, changes of this sort do not take place. For example, with many substances, particularly with hydrates in solution, if we carefully remove all traces of the solid solute, we may cool a solution much below the point where crystallization should occur without any change manifesting itself. This we have already encountered (see Supersaturated Solutions, Chap. IV). Such systems are said to be in **metastable equilibrium**. The phenomenon is of quite frequent occurrence. For example, water may be cooled much below zero without formation of ice. Rhombic sulfur may be heated much above the transition point,  $94.5^{\circ}$  (see Fig. 67) without immediate transformation to the monoclinic form. Gas may be cooled below or compressed beyond the true equilibrium point before liquefaction begins. Ordinary "taffy" and "butterscotch" are metastable solutions of sugar. If, however, we have a metastable system and initiate the change to a stable form the change always goes on until the true equilibrium is obtained. Initiation of such changes is usually easy. The methods ordinarily effective are violent agitation of the system or "inoculation." Inoculation consists in introducing into the system a small amount of the phase tending to be formed. Why these means should effect the change is not known.

**Cryohydrates or Eutectic Mixtures.**—When solutions of salt and water are cooled the freezing point of the solution is lower than that of pure water, as we have already observed. If the solution is dilute, pure ice separates out. This, of course, leaves the remaining solution more concentrated and on further cooling the ice continues to separate until a concentration of 22.4 per cent is reached. The whole then solidifies. If a concentration of salt in solution greater than 22.4 per cent be cooled, salt crystallizes out on cooling until again when 22.4 per cent is reached the whole solution crystallizes. This is graphically illustrated in Fig. 68. The point  $O$  corresponding to  $-21.2^{\circ}\text{C.}$ , and a concentration of 22.4 per cent salt is known as the eutectic point. This was supposed to correspond to the freezing point of a hydrate,  $\text{NaCl} \cdot 10\text{H}_2\text{O}$ , hence the solid was called a cryohydrate (from  $\kappa\rho\upsilon\sigma$  = frost). Such solids do not consist of transparent crystals but are opaque. One of the components is frequently soluble in a solvent which does



not affect the other. It is usually not possible to express the composition in terms of simple multiples of the atomic weight. For these reasons these solids are considered as mixtures and

termed **eutectic mixtures** (from *εύ* = easily and *τῆκεν* = to fuse). The most convincing reason for considering them mixtures is that according to the phase rule such a system should be, as it is, non-variant.

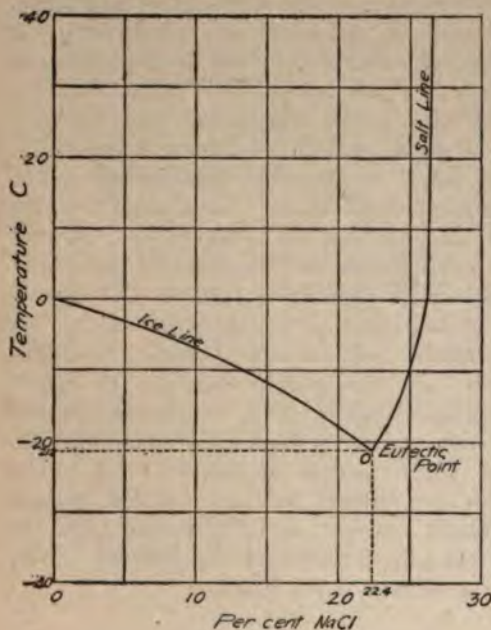


FIG. 68.

**Maximum Points in Freezing Point Curves.**—Two examples of the application of the phase rule to the detection of compounds may now be given. If we add gaseous hydrochloric acid to water the freezing point is lowered until a eutectic point, at  $-85^{\circ}$ , is reached. (See Fig. 69.) By increasing the concentration of the

acid the freezing point is raised until at  $-24.4^{\circ}$  we have a maximum point in the freezing point curve. The concentration of acid is at this point 40.3 per cent HCl. This corresponds to a compound of the formula  $\text{HCl} \cdot 3\text{H}_2\text{O}$ . Now, by the phase rule, if there exists but one component and three phases, we should have a non-variant system and hence no degrees of freedom ( $3 + F = 1 + 2$ , therefore  $F = 0$ ). It further follows from the phase rule that addition of either water or acid to this system should lower the freezing point, and this is the case. The occurrence of maxima in freezing point curves is hence considered as indicative of compounds formed between solute and solvent just as minima indicate eutectic mixtures. The maxima in the curve given in Fig. 68 correspond to  $\text{HCl} \cdot 3\text{H}_2\text{O}$  and  $\text{HCl} \cdot 2\text{H}_2\text{O}$ . There is, however, no maximum corresponding to the composition of the constant boiling solu-

tion of hydrochloric acid (*cf.* p. 126), which is an additional reason for regarding this solution a mixture.

A similar set of maxima in the freezing point curve of sulfur trioxide and water are given in Fig. 70. They correspond to the hydrates  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_7$ . Other examples of such utilization of the phase rule might be cited. They will be more effective, perhaps, if considered separately.

#### Freezing Mixtures.

— When ice and salt are mixed, since some salt dissolves in the moisture upon the surface, we have a system consisting of four phases, ice, salt, solution and vapor and but two components. Such a system is non-variant ( $4 + 0 = 2 + 2$ ). The only point where equilibrium can be reached is the eutectic point. Since ice in melting absorbs heat the temperature is continually lowered and, if there is an excess of salt and the system is sufficiently isolated, the eutectic point  $-21.2^\circ$  is reached.

With any other mixture of ice and a soluble substance a like lowering of the temperature is produced, provided, of course, the heat of solution is not greater than the absorption produced by the melting of ice. The minimum temperature is, of course, the cryohydric point for the substance used. Whether this temperature is actually reached depends on the quantities used and the completeness of insulation of the system. One of the most remarkable freezing mixtures is that furnished by ice and sulfuric acid, by means

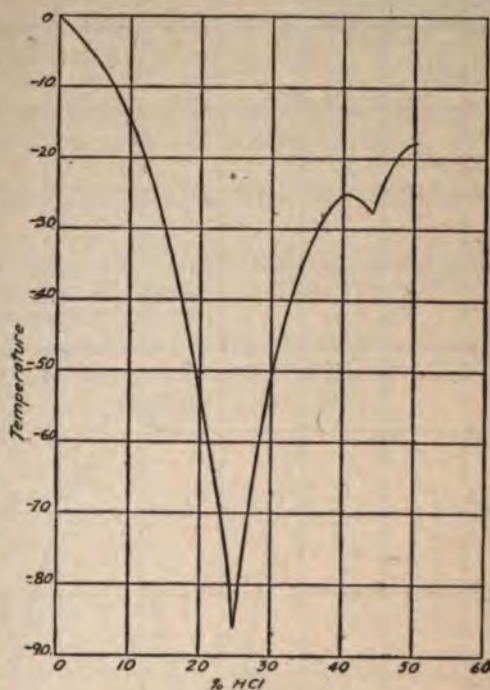


Fig. 69.



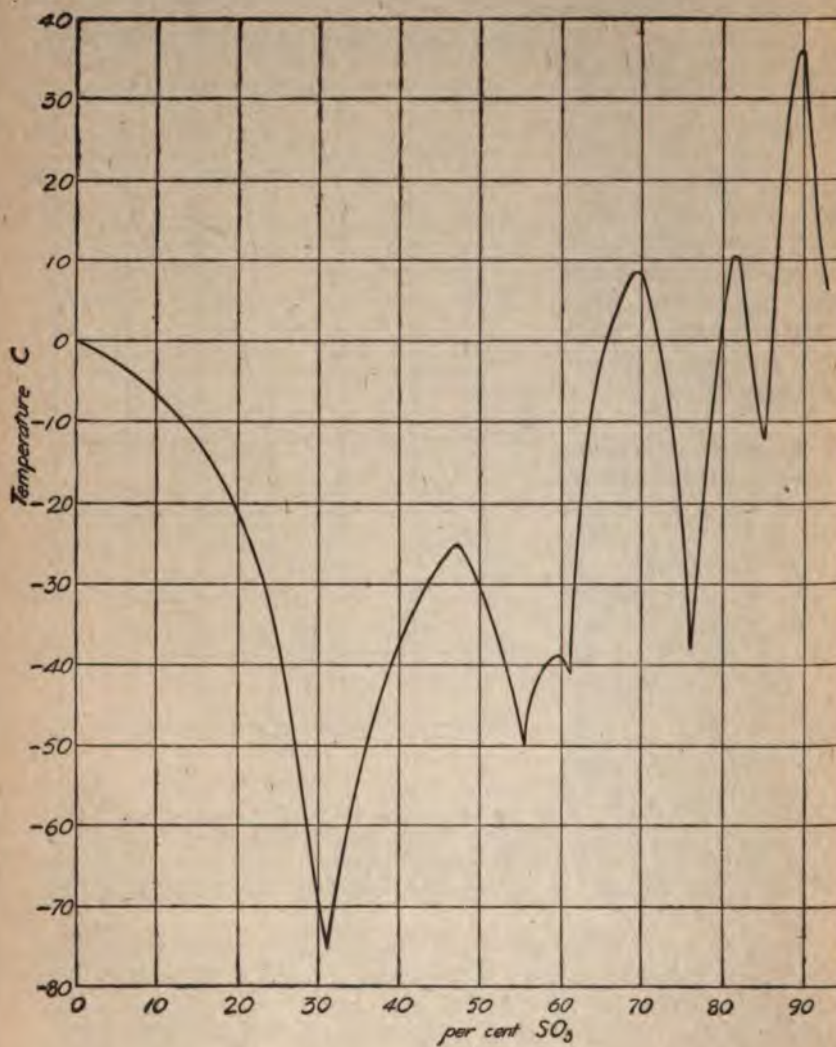


FIG. 70.

of which a temperature of  $-37^{\circ}$  C. is readily obtained. With  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and ice a temperature of  $-55^{\circ}$  C. is obtained. The use of freezing mixtures for the manufacture of ice cream and other uses is very familiar. Another long used application is in the liquefaction of ice on sidewalks by use of salt or of ashes.

**Exercises.** — 1. Under what circumstances could a non-variant system consisting of sodium sulfate and water exist? A univariant system?

2. How could you prepare a metastable system of sodium thiosulfate and water?

3. Show by the phase rule that the maxima and minima in freezing point curves of aqueous solutions of hydrochloric acid and sulfuric acid constitute non-variant points.

4. When potassium iodide solution dissolves iodine it is possible that either  $\text{KI}_3$  or  $\text{KI}_5$ , or both, are produced by addition. Could the phase rule be used to solve the problem? If so, how?



## CHAPTER XIV

### NITROGEN AND AMMONIA

**Introduction.**—We have observed that certain elements in each group of the periodic system are very clearly related to each other, but we have not discussed any members of sub-group *A*. This is partly because of the greater importance of the members of the sub-group *B* and partly because the members of sub-group *A* of both the sixth and seventh groups have properties relating them with metals. Their discussion will be presented in due season. It seems wise at this stage to take up a new group and present its typical element in some detail and then, in less detail, the sub-group *B* related to it. There is also a very important substance, the air, which must find discussion somewhere because of its importance, and yet no rational place is set aside for discussion of mixtures. Hence, we shall introduce it along with its most important component (see Chap. XV),

**Occurrence.**—In the free condition nitrogen constitutes approximately four-fifths of the air. This statement, brief as it seems, is sufficient to convey to the reader the realization of the enormous quantity of the substance available in this form. Since, as we shall see, nitrogen in proper combinations is an essential food-stuff, this potential reservoir is interesting (*vide infra*). It is also found occluded or enclosed in some minerals. Combined, it is found in many forms, for example, ammonia and nitrates are present in small quantities in all fertile soils and great deposits of nitrates are found in dry regions such as northern Chile and the Death's Valley region of California. Natural manures, such as guano, contain nitrogen compounds. Most important of all, whenever living matter endowed with the power of auto-locomotion, is found, nitrogen compounds of the order of albumin are present, and it is interesting to note that whatever the exact character of this substance may be the percentage of nitrogen is always nearly the same, 15 per cent.

**History.**—Nitrogen was in an uncertain manner recognized as an inactive constituent of the air at least a hundred years before Rutherford, in 1772, recognized that by burning substances in the air a residue incapable of supporting combustion was left. Lavoisier proposed to call this gas azote (from  $\alpha$  = not and  $\zeta\omega\rho\acute{o}s$  = living). Chaptal (1823) suggested the name nitrogen (from  $\acute{\nu}\iota\tau\rho\omega\nu$  = niter and  $\gamma\acute{\epsilon}\nu\alpha\omega$  = I produce). This name is used by English-speaking peoples. The Germans use the highly descriptive term stickstoff (= choke stuff). Yet in all languages the symbol is N except in the French. This is interesting as presenting almost the sole exception to the international symbolism of chemistry.

**Preparation.**—Somewhat impure nitrogen may be prepared from the air by burning easily combustible materials, such as phosphorus, in suitable closed vessels and absorbing the products of combustion in water. (Fig. 71.) If the residual gas is then passed through an alkaline solution and subsequently over a drying agent such as phosphorus pentoxide, the process removes the oxygen, carbon dioxide and water vapor and leaves an inactive gaseous mixture consisting of about one per cent of a mixture of gases known as the argon family and of nitrogen.

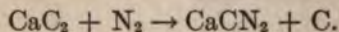
Pure nitrogen may be prepared by gently heating ammonium nitrite:  $\text{NH}_4\text{NO}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2$ . It is more convenient, usually, to heat ammonium chloride and sodium nitrite, thus forming and immediately decomposing the nitrite of ammonium. Of course, many other methods of isolation of nitrogen, more or less pure, are available, such as the decomposition of ammonium dichromate by heat, decomposition of ammonia by heated copper oxide, fractional distillation of liquid air, etc. The last mentioned is used where large quantities of nitrogen are used in manufacturing operations, as in the manufacture of cyanamide.



FIG. 71.



**Properties, Physical and Chemical.**—Nitrogen is a colorless, odorless, tasteless gas, soluble in water only to the extent of two volumes per 100 at 0°. It may be condensed to a liquid, which boils at -195°, and forms by further cooling a snow-like mass with a melting point of -214°. Its molecular weight is 28.02, and its specific gravity is 0.967. One liter under standard conditions weighs 1.2506 grams. It is, at ordinary temperatures, an inactive gas and unites very slowly, if at all, with other elements. This inactivity is usually regarded as due to the stability of its molecules in diatomic form. At any rate, when subjected to such treatment as would tend to dissociate it into its atoms, for example, at high temperature or under the influence of the electric spark, it reacts fairly rapidly with many elements and compounds. Thus if heated to a high temperature with certain metals, as calcium, lithium, magnesium, etc., it forms compounds known as nitrides. Also if nitrogen is heated in an electric furnace with calcium carbide,  $\text{CaC}_2$ , a highly valued fertilizer is produced, known as cyanamide,  $\text{CaCN}_2$ ,



If nitrogen be sparked with oxygen, some nitrogen peroxide is produced, and if the establishment of equilibrium be prevented by absorption of the oxide in water or alkali, the reaction may be made complete. This reaction was used by Cavendish in 1785 and in the last few years, due to cheap electric power and a special process, known as the Birkeland-Eyde process, has been used to prepare tons of nitrates. (See Eighth International Congress Report, Vol. 28, p. 169.) If hydrogen be used instead of oxygen, the union of the two elements proceeds very slowly at higher temperatures and equilibrium is reached before a very large proportion of the gases unite, but by means of high pressure the reaction,  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , may be shifted toward the right, as is to be expected from Le Chatelier's Law. If the reaction be hastened by means of a catalytic agent the process may be used in the manufacture of ammonia, as is being done by the Badische Anilin und Soda Fabrik (*cf.* p. 265) (see Jour. Ind. and Eng. Chem. Sept. 15, 1917). If nitrogen is enclosed in tubes and evacuated until a low pressure is reached and "sparked" by static discharge an active form of nitrogen is obtained, which unites directly with phosphorus, sodium, mercury, etc., at ordinary temperatures

It is supposed by its discoverer, J. R. Strutt, to be monoatomic nitrogen, but this is by no means certain.

The equivalent weight of nitrogen, as shown by analysis of ammonia, is 4.67, and the smallest proportion which appears in a gram molecular volume of any of its volatile compounds is 14.01. In ammonia it is, therefore, a trivalent element. As will be seen, we have reason to believe that it always shows this valence with hydrogen alone, though in combination with other elements its valency may vary from one to five.

**Uses of Nitrogen.—The Nitrogen Cycle.** Nitrogen is an essential constituent of all living forms of matter and is constantly being built into new tissues and being removed as old tissues are destroyed incident to functional activities. It is, therefore, essential as both plant and animal food, and it is present in various forms in the products of decay. Yet animals, and plants in general, are unable to use atmospheric or other free nitrogen and animals cannot assimilate the so-called mineral compounds. Animals are dependent upon plants, directly or indirectly, for their supplies of nitrogenous food, as well as for their supplies of combined carbon. (See carbon cycle.) Plants are ordinarily able to use nitrates and other nitrogen compounds and from them produce the complex forms which are available both for plants and animals as food.

The single instance of direct utilization of atmospheric nitrogen by living organisms seems to be furnished by certain bacteria which thrive best, apparently, upon the roots of certain plants. (This sort of community life is called symbiosis.) These bacteria appear to be able to convert atmospheric nitrogen into forms available for their own use and, directly or indirectly, a supply available for their hosts, a sort of rent as it were for the nodules furnished by the peas, beans, clover, etc., with which they live.

When nitrogen in the form of compounds has served its function in the living body and is removed as excreta, or the animal or plant decays after death, the further course depends upon circumstances. If decay takes place out of contact with basic materials, the putrefactive organisms convert the nitrogenous compounds into ammonia, which is either absorbed by the soil and is again available for plant food, or it escapes into the air to be eventually returned to the soil through the agency of rain. Under certain circumstances, apparently dependent upon

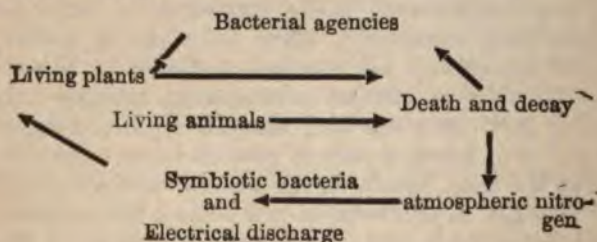


the presence of basic materials such as potassium, sodium, and calcium carbonates and phosphates and certain varieties of bacterial organisms, the effete organic nitrogen is converted into nitrates, which are available as plant food.

When such refuse matter is burned, most of the nitrogen is returned to the air in elementary form, and, so far as natural processes are concerned, is forever lost to living forms, except such relatively small amounts as are again rendered available by lightning flashes forming oxides of nitrogen, and by the bacterial agency previously mentioned.

Sewage which is allowed to escape into the sea also escapes utilization, at least in large part, and hence the modern garbage incineration and sewage disposal has its unfortunate, as well as its advantageous, aspects. This theme might be more extensively discussed with profit, but this is perhaps not the place. Bunge's idea that all operations which destroy nitrogenous compounds, such as the explosion of dynamite and guncotton and destruction of sewage and garbage, are destructive of life, whatever their immediate result, is worthy of thought. These operations are mostly human activities, and the counteracting influences are the artificial manufacture of nitrogen compounds from the air such as are mentioned on p. 264. This is a particularly interesting illustration of the theorem of Le Chatelier.

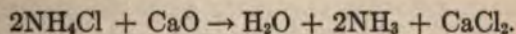
The figure below, modified from Mellor, illustrates graphically the cycle of nitrogen in nature.



#### AMMONIA AND ITS DERIVATIVES

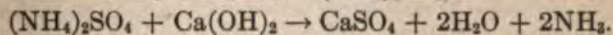
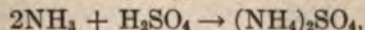
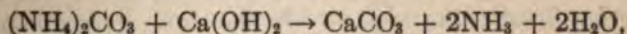
**Occurrence.** — As is obvious from the cycle just discussed, ammonia, or its derivative compounds, is present in the atmosphere in small and varying quantities and also in surface waters. It may be detected in the gases rising from decaying animal refuse and is a constituent of most volcanic gases.

**History.** — Ammonia, or rather ammonium chloride, was known to the early alchemists, being formed by the distillation of urine, or the dejecta of animals, with common salt, hence the name *spiritus salis urinae*. The name sal ammoniac seems to be derived from the fact that it, ammonium chloride, was known to the priests of Ammon, the Sun God of Egypt. A pungent ill-smelling liquid containing ammonia was early obtained by distilling harts' horns collected in the forests of Europe. It was used medicinally, and was called spirits of hartshorn. The gas was first collected in a pure condition by Priestley in 1774, by distilling ammonium chloride with lime and collecting the gas over mercury. He called it alkaline air.



Its composition was established by Berthollet (1783) and its volumetric relations by Gay-Lussac (1808).

**Preparation.** — (1) When coal is distilled, for the preparation of coal gas or of coke, huge quantities of ammonia and of ammonium salts are formed. These are also formed when any similar nitrogenous material is subjected to destruction by distillation. Ammonia and ammoniacal compounds are found in the aqueous distillate. By distilling this liquid with slaked lime, or other bases, ammonia is liberated and may be absorbed by dilute sulfuric acid. When a quantity of sulfuric acid is neutralized the solution is evaporated to crystallization, and the crude sulfate so obtained is again distilled with lime. The reactions taking place may be illustrated:



The details of the very elaborate machinery used in carrying out these operations on a large scale may be obtained from books on Industrial Chemistry. (See Thorpe's Industrial Chemistry.) The ammonia so obtained may be compressed into liquid form and stored in suitable steel cylinders, or it may be absorbed by water; in which form it is sold as *aqua ammonia*.

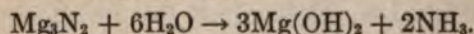
(2) Ammonia may also be formed by reduction of the oxygen compounds of nitrogen by nascent hydrogen. The most convenient illustration is furnished by placing zinc or aluminium in



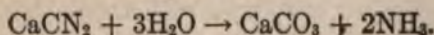
a solution of sodium hydroxide and to the mixture, which slowly evolves hydrogen, adding a solution of a nitrate. The ammonia formed may be driven off by distillation and the quantity determined by any suitable method. (See Nessler's Reagent.) This method is interesting because it may be used for determining the quantity of nitrates in water and sewage.

(3) Ammonia is also formed when organic compounds are heated with concentrated sulfuric acid. Of course, ammonium sulfate is at once formed; and the ammonia, if desired, has to be liberated by distilling with a base. If the formation of ammonia is to be quantitative, *i.e.*, if all the nitrogen is to be so transformed, various modifications have to be made. These are fully discussed in all texts on quantitative chemistry, since the method, known as Kjeldahl's method, is most frequently used in determining the nitrogen content of foods and other articles of commerce.

(4) Ammonia is formed by the reaction between water and certain nitrides (hydrolysis), *e.g.*,



This type of formation is important because it is similar to that which takes place slowly in the soil with calcium cyanamide and gives to the latter its value as a fertilizer.



(5) As previously mentioned (p. 133), ammonia is formed by sparking a mixture of nitrogen and hydrogen together, but the action is slow and reversible. It may be driven to completion in case ammonia is removed as fast as formed, but so far the method has not been found practicable on a large scale. If, however, nitrogen and hydrogen be brought together at high temperature and pressure, in the presence of a catalytic agent, *e.g.*, at 500° C. and 210 atmospheres of pressure, and with osmium as a catalytic agent, the reaction may be made to go rapidly and readily enough to furnish the basis of a process of commercial preparation of ammonia.

This is a very recently developed industry, and is especially remarkable not only because the difficulties of operating with huge volumes of gas at high temperature and high pressure are very great, but also because of the fact that the product is a cheap commodity and the cost of operation and of the catalyzer would seem prohibitive. (Ammonia costs about 0.007 of a cent and osmium about \$2 per gram.) The industry is also remarkable because the nitrogen needed for the

process is obtained by fractionation of liquid air (*q.v.*) and the hydrogen by fractionation of liquid water gas (*q.v.*). Its development is supposed to have a very great bearing upon Germany's ability to supply itself with war munitions, because ammonia is not only a factor in certain explosives (see ammonite) but the gas may be burned, in the presence of platinum as a catalyzer, to produce nitric acid, a very essential factor in the production of explosives. It is claimed that over 100,000 tons of nitric acid were produced by this method in Germany in 1915, and that the German government has subsidized the industry to the extent of fifty million dollars. (See *English Review*, Vol. 22, p. 22, 1916.) The success of this commercial enterprise is an example of the human ingenuity which almost justifies Shelley's poetic frenzy in his *Ode to Man* in "Prometheus Unbound":

"The lightning is his slave; Heaven's utmost deep  
Gives up her stars and like a flock of sheep  
They pass before his eyes, are numbered and roll on:  
The tempest is his steed, he strides the air;  
And the abyss shouts from her depth laid bare,  
Heaven hast Thou secrets? Man unveils me, I have none."

(6) In the laboratory when small amounts of ammonia are desired, the most convenient method is to gently warm the concentrated solution, aqua ammonia, and pass the gas, for drying, through a U tube or other gas drying tube filled with pieces of quicklime (CaO). (See Fig. 17.)

**Properties.** — Ammonia is a gas at ordinary temperatures with a pungent odor which is quite characteristic. It is non-respirable and affects painfully the membranes of the eyes and throat. Its specific gravity is 0.5971 and it must be collected over mercury or by air displacement, since it is so very soluble in water. When subjected to pressure it is liquefied and the liquid boils at  $-33.5^{\circ}$ . Its critical temperature is  $131^{\circ}$ . The heat of evaporation of the liquid is 5700 cal. for 17 grams. These relations are especially important because they are the basis of operation of most ice making plants, cold storage plants and other commercial operations in which refrigeration forms a part.

If ammonia be subjected to sufficient pressure and the temperature rise caused by the concentration and liquefaction be removed by passing the gas through condensers kept cool by flowing water, the liquefied gas may be collected and stored in cylinders. These cylinders must be sufficiently strong to withstand any pressure likely to be caused by the rise of temperature of the liquid in transportation or use. These pressures are at

$-33.5^{\circ}$	$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$30^{\circ}$
15.7	65.8	88.25	123.5	167.6 lbs.



If the liquid be allowed to expand into gaseous form, heat must be absorbed equal to that produced in liquefaction. If the apparatus be so constructed that the conversion to gas takes place in pipes surrounded by brine the latter will be cooled. If brine so cooled is then pumped into pipes distributed about rooms the same effects, reversed, will be produced, as in heating rooms with steam pipes. That is, the room temperature will be lowered. By proper distribution of refrigeration surface exposed and of the rate of flow and temperature of the brine any required temperature between the cryoscopic point of brine and the outside temperature may be maintained. This method of cooling rooms is in operation in cold storage plants for preservation of meat, fish, eggs, fruit, etc., in breweries, wine cellars, office buildings, etc. If instead of pumping the brine for room cooling purposes vessels of water are immersed in it the water may be converted to ice. The value of this operation for the comfort and health of tropical and semi-tropical residents can scarcely be estimated and its effects on standards of living and commercial activities is wonderful. To trace its effects on health, commerce, cost of living, political conditions, etc., would require vast research and many pages, so we forbear. It is to be recalled that any other liquefied gas in general may be similarly employed and the reasons that ammonia and sulfur dioxide occupy the field to the almost exclusion of others are the commercial considerations of total cost of materials and manipulation. For details of machines and devices employed see any standard work on industrial chemistry.

Liquid ammonia is in appearance similar to water. By employing Dewar flasks (*q.v.*) the liquid may be used instead of water

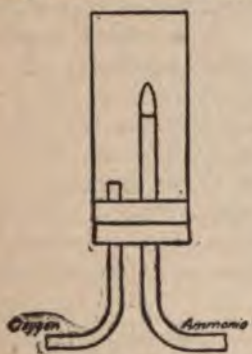
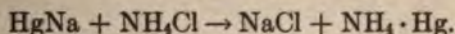


FIG. 72.

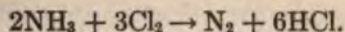
for many operations. Franklin has brought to light many interesting reactions which take place when liquid ammonia is used as a solvent and that the ions it produces are different from those produced by water. (See Jour. Amer. Chem. Soc., Vol. 27, p. 192, 820, and Amer. Chem. Jour., 20, 820.) Ammonia does not support combustion of ordinarily combustible substances nor does it burn in air, but if an atmosphere of pure oxygen be provided as shown in Fig. 72, ammonia will burn with a yellowish flame, forming water and nitrogen and small quantities of nitrogen peroxide. (See also p. 265.)

Ammonia unites with many substances to form crystalline compounds analogous with the crystalline hydrates, which are said, therefore, to contain ammonia of crystallization. Examples are the salts  $\text{CaCl}_2(\text{NH}_3)_6$ ,  $\text{CuSO}_4(\text{NH}_3)_4$ , etc. For this reason calcium chloride is not suitable as a drying agent for ammonia.

Ammonia unites by addition with all acids, at least if a trace of water is present, forming salts known as ammonium salts, which ionize, furnishing the ion  $\text{NH}_4^+$ , which acts as if it were a metal, hence the name ammonium. This hypothetical metal has never been isolated, though when ammonium chloride is treated with sodium amalgam (the latter made by dissolving sodium in mercury), an amalgam-like mass of unstable character is produced, which is supposed to be an amalgam of the radical  $\text{NH}_4$ :



The amalgam, if formed, decomposes rapidly into mercury, ammonia and hydrogen. Ammonia reacts readily at high temperatures with certain metals, forming either nitrides by complete displacement of the hydrogen as, for example,  $3\text{Mg} + 2\text{NH}_3 \rightarrow \text{Mg}_3\text{N}_2 + 3\text{H}_2$ , or substituted compounds, known as amides, as  $\text{Na} + \text{NH}_3 \rightarrow \text{NaNH}_2$ . Both the nitrides and amides are decomposed by water (*cf.* p. 264). Ammonia is also decomposed by the halogens, *e.g.*,



If an excess of chlorine be added to a warm solution of ammonium chloride an oily yellow substance, nitrogen trichloride ( $\text{NCl}_3$ ) is formed. It explodes violently upon the slightest provocation — and, indeed, apparently without provocation, *i.e.*, spontaneously. Its formation and decomposition may be simultaneously demonstrated by the electrolysis of ammonium chloride. A similar, though not quite analogous compound, is formed when ammonium chloride solutions are treated with iodine. The chocolate brown insoluble substance is apparently  $\text{NI}_3$ , mixed with  $\text{NH}_2\text{I}$  and  $\text{NHI}_2$ . Some prefer to regard it as having the composition  $\text{N}_2\text{H}_3\text{I}_3$ , *i.e.*,  $\text{NH}_3 \cdot \text{NI}_3$ . In any case, it is an extremely entertaining substance, if handled discreetly. It is not very unstable if damp, but if dry explodes violently even under the shock of a pulse of air passing over it.

Ammonia dissolves very readily in water, the maximum solubility at  $0^\circ$  being 1298 vol. to one. As the temperature rises the solubility decreases until at  $20^\circ$  the solubility is about 700 : 1. The solution, the aqua ammonia of commerce, is formed with evolution of heat and expansion of volume, the specific gravity of the ordinary "concentrated ammonia" being 0.90 and containing 28 per



forming salts with acids by addition, as  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , instead of by neutralization.

**Positive and Negative Valence.** — A very interesting valence relation manifests itself in hydroxylamine. The hydroxyl group is ordinarily negative and when it combines with any element neutralizes a positive valence of that element. In hydroxylamine, however, it appears to be a positive radical and to neutralize the negative valence of nitrogen. This reaction has an interesting bearing upon the electron theory of valence. (See L. W. Jones, Jour. Am. Chem. Soc., Vol. 36, p. 1268.)

Nitrogen trichloride also offers an interesting valence relation. If the trichloride is hydrolyzed we get  $\text{NCl}_3 + 3\text{HOH} \rightleftharpoons 3\text{HOCl} + \text{NH}_3$ . This decomposition indicates that in the trichloride chlorine acts as a positive element. (For a fuller discussion of this relation see Jour. Am. Chem. Soc., 35, 767.)

**Exercises.** — 1. Calculate the weight of nitric acid which could be produced from the nitrogen present over one square meter of the earth's surface when the barometer is at 760 mm., assuming the percentage by weight of nitrogen to be 75.5% of the atmosphere.

2. What is the weight of a gram molecular volume of air which has 21% oxygen, 78.1% nitrogen and 0.9% argon by volume?

3. Design an apparatus to prepare nitrogen from air by using copper to absorb the oxygen. If iron were to be used instead of copper, what preliminary treatment of the air would be necessary? Why?

4. Explain in detail why nitrogen should show chemical activity at high temperatures if its inactivity at ordinary temperatures is due to its molecular stability.

5. The products of the distillation of coal are gases, water, tar, and coke. Can you explain why the first distillation gives a "crude sulfate"?

6. Explain what is meant by nascent hydrogen (p. 263). Why is it more effective than would be a stream of gaseous hydrogen?

7. What is the ratio of initial to final volume in the decomposition of ammonia by sparking if the dissociation is 94%? How will increase of pressure affect the point of equilibrium?

8. What is the weight of ammonia in a liter of aqua ammonia

of specific gravity 0.90? Express the concentration in terms of normal solution. What is the ratio of the weight of water to ammonia?

9. If on conversion of 1 gram of liquid ammonia at  $0^{\circ}$  to gas at  $0^{\circ}$ , 294 calories of heat are absorbed, what quantity must vaporize to freeze 1 kilogram of water at  $0^{\circ}$ ? Of sulfur dioxide with absorption of 91 calories per gram? Of chlorine with absorption of 67 calories per gram? If the costs of the liquid are in the ratio 3 : 2 : 1, which is the cheapest raw material for ice manufacture?

10. If ammonium chloride dissociates when heated,  $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$ , can you suggest any means by which ammonium chloride could have its molecular weight determined?



## CHAPTER XV

### THE ATMOSPHERE AND THE ARGON FAMILY

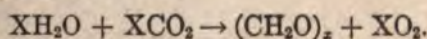
THE gaseous envelope of the earth is called the atmosphere ( $\alpha\tau\mu\acute{o}\varsigma$  = vapor,  $\sigma\phi\alpha\acute{\iota}\rho\alpha$  = sphere). It or any portion of it is commonly called the air ( $\alpha\epsilon\rho$  = to breathe). It was one of the elements of Aristotle and in spite of the demonstration by many investigators of the existence of varieties of air-like substances such as *inflammable air*, hydrogen, *fixed air*, carbon dioxide, and despite the observation of Boyle that "perhaps there is scarcely a more heterogeneous body in the world," it continued to be regarded as an element until the discovery of oxygen by Priestley, and the demonstration of its relation to the air by Lavoisier.

**Essential Factors.**—The various factors, many in number, which go to make up the whole may, for the convenience of the present discussion, be divided into two groups: essential, that is to life, and non-essential. Oxygen and nitrogen and their essential relation to living organisms have been already discussed. The constancy of the relative amounts of these factors is very interesting in view of the fact that there are so many means of removal, such as decay, combustion, animal respiration, oxidation of metals, etc. The compensating factors are discussed below. That the relative quantities are constant is shown by the fact that the mean value of a series of very accurate analyses, 165 in number, made at Paris, Cape Horn and Cleveland, Ohio, show a mean value of 20.94% oxygen, while the maximum values were 20.999% and the minimum 20.72%. Considering the unavoidable experimental errors, this indicates practical, though not quite absolute, constancy. The corresponding quantity of nitrogen is 78.05% by volume. The weight relations are 23.15% of oxygen and 75.52% of nitrogen. These figures, of course, refer to dry air.

Water vapor is, of course, an essential factor of the air, but is present in quantities which vary from hour to hour. The

quantity is increased by evaporation from water and moist surfaces, by the exhalation of moisture from the leaves of trees and by the respiratory processes of animals. It is decreased by lowering of temperature and consequent precipitation in the form of dew, rain and fog. In regions of fairly frequent rainfall, the amount present averages about two-thirds the vapor tension of water for the temperature. The range is very great. Two popular misunderstandings may here be mentioned. When the atmosphere has a humidity of 100%, i.e., when the vapor pressure of moisture corresponds to the vapor tension of water at the same temperature, and when any lowering of the temperature must cause precipitation, the air is said to be "saturated" with moisture. It should be remembered that the presence or absence of the other factors of air in nowise affect the situation. The amount present depends solely upon the relation between water and its vapor. The expression "a heavy atmosphere" when the humidity is high is peculiarly inapt, since it follows from Avogadro's principle that atmosphere composed partially of water molecules weighing 18 must be lighter than that made up wholly of molecules of nitrogen and oxygen whose mean weight, considering relative volumes, is 28.955. This is also in harmony with the low barometer, which invariably accompanies high humidity. The feeling of lassitude which accompanies high humidity is undoubtedly to be attributed partially to the lower percentage of oxygen in moist air, and partially to the low rate of body evaporation under the same circumstances.

Carbon dioxide, though present in relatively small quantities in the air, must be considered an essential factor, since all plant life, and hence indirectly animal life, depends upon it. The plants consume carbon dioxide and liberate oxygen, thus maintaining the supply of the latter:



The reaction indicated takes place only in the presence of the chlorophyll of plants under the influence of the sunlight. Most of the operations which deplete the oxygen supply furnish carbon dioxide and water, and so the greatest equilibrium reaction in nature is kept in a fairly constant balance. The quantity of carbon dioxide ordinarily is 0.04% by weight and 0.03%, or 3 parts per ten thousand, by volume; and by diffusion, wind movements, etc., is kept wonderfully constant. Of course, locally, as in in-



habited rooms, or in cities during foggy, or otherwise quiet weather conditions, the proportion may rise to 7 or 9 parts to 10,000 and in rooms very badly ventilated, even to the point where discomfort may ensue, due to lack of oxygen. Usually, however, the discomfort due to lack of ventilation is caused by other substances exhaled, and by the increased humidity of the air. It has been shown that even 400 or more parts per 10,000 may be inhaled without discomfort if the carbon dioxide is pure.

Carbon dioxide is being continually converted into soluble compounds by reaction with silicate rocks to form soils (*q.v.*) and these soluble compounds, mostly sodium and potassium carbonates, eventually find their way to the sea and are there converted to calcium and magnesium carbonates, which are insoluble. This reaction probably is very slowly depleting the available supply of carbon dioxide.

**Non-essential Factors.** — Air usually contains small quantities of a large variety of substances of which the most important in quantity are the members of the argon family of elements (*vide infra*). Of the others perhaps the most important is dust. This varies both in quantity and character, according to the locality, but is never wholly absent. The number of particles ranges from 32,000, under most favorable conditions, to many millions per cubic centimeter. These suspended particles consist of portions of soil carried into the air by winds, the constant output of volcanic activity, the spores of fungi, bacteria, coal dust, ashes, coal smoke, etc. The organic particles give rise to the so-called "spontaneous fermentation" of exposed fruit juices, to air-borne diseases, to infection of exposed wounds, etc. It is probable that to dust we owe the blue color of the sky. It is also probable that were no dust particles present in the air formation of rain drops would be impossible, since particles of some sort are required as nuclei about which drops may form. (See Dust, Enc. Brit.)

Hydrogen is present in air to the extent of about 1 part per 100,000. In cities, especially, there are still smaller amounts of hydrocarbons, which are probably produced by imperfect coal combustion. The presence of unusual quantities of these substances accounts for the ill health of city vegetation, since the stomata of leaves have their respiratory functions interfered with by deposits of such materials. Oxides of nitrogen, and conse-

quently nitric acid; ammonia and consequently ammonium nitrate are also present in small amounts. These being soluble in water are continuously removed and doubtless are a factor in soil fertility. The combined nitrogen so returned to the soil per year has been estimated to amount to as much as six pounds per acre.

Both ozone and hydrogen peroxide are formed in the air by electrical disturbances and the latter may be a constant, though very small, factor. No adequate evidence of the continuous existence of the former is at hand, the health resort advertisements to the contrary notwithstanding. Of course, in local conditions various other substances may occur. Thus air near the sea may, especially in stormy seasons, carry mechanically considerable quantities of salt. The neighborhood of factories may contain various gases or finely divided solid outputs of the same. These, as in the case of sulfur dioxide, cement dust, hydrochloric acid, etc., may become at times the subject of very perplexing and bitter legal controversies.

#### THE ARGON FAMILY

The most interesting, though perhaps least important, of the minor air factors are collectively known as the argon family. Their interest from the scientific point of view and their properties may as well be presented through the story of their discovery. In the years 1893-1895, Lord Rayleigh, an English physicist, discovered that nitrogen obtained from the air in as pure a state as possible, by removal of moisture, dust, oxygen, etc., weighed, under standard conditions, 1.2572 g., while that, prepared from ammonium nitrite and other substances through decomposition by heating, weighed but 1.2505 g. per liter. The actual corrected weights used were 0.14332 g. for "nitrogen" from the air and 0.14256 g. for "artificial" nitrogen and this difference, slight as it was, being greater than was to be accounted for by the errors of the experiment, led to the isolation of a whole family of elements. Hence this discovery is called the "Triumph of the fourth decimal place." With the assistance of William Ramsay, the cause of this difference was ascertained to be the presence in the air of a gas which is slightly heavier than nitrogen. It was freed from nitrogen by passing the mixture over heated magnesium, or, better still, calcium, with which nitrogen unites, leaving a residue of gas, which is wholly inert chemically and



cannot be induced to enter into combination by any known means. Hence it was called argon (*ἄργος* = idle, lazy). It is interesting to note that in 1785 Cavendish had observed that when nitrogen is sparked with oxygen and the resulting oxide dissolved in alkalis there remains a residue incapable of combination. However, this observation was not fruitful.

During the years in which Ramsay was pursuing the investigation of argon, liquid air (*vide infra*) became available, and the fractional evaporation of liquid air was found to be a convenient method of obtaining the gas. When liquid air is allowed to evaporate the last portions are rich in argon and also, as Ramsay found, this residue contained small quantities of two other gases, likewise chemically inert and called krypton (*κρυπτός* = hidden) and xenon (*ξένος* = stranger).

In his search for other sources of these gases Ramsay was led to investigate gases which were evolved from certain minerals, notably cleveite, when dissolved in acids and which by reason of chemical inactivity were supposed to be nitrogen. The quantities of gas so obtained were small and a convenient method of examinations was by means of the spectroscope (*q.v.*). Instead of showing the characteristic lines of either nitrogen or argon only, these gases revealed a spectrum similar to certain lines in the spectrum of the sun's photosphere, which had been observed by Janssen and by Lockyer and regarded as evidence of a solar element which it was proposed to call helium (*ἥλιος* = sun). Later Ramsay was able to isolate this gas by collection of the *first* fraction of liquid air and hence prove its presence in the air.

These gases, argon, helium, krypton and xenon, were all inert and evidently, therefore, chemically similar. Their molecular weights were respectively helium = 4; argon = 39.9; krypton = 82.93; xenon = 130.2. As we shall shortly see, they being monatomic, have also the same atomic weights and evidently constitute a family of the periodic system and indeed form a transition group between the acid forming and base forming elements. It will be noted that so far we have made no mention of the element which should occupy the space before sodium. This vacant pew, "*soi disant*," was noted by Ramsay and, after a thrilling search through earth, waters and stars, was filled by the isolation from the air of a gas having the required properties and whimsically named neon (*νέος* = new), the baby as it were. (See Ramsay and Travers, *Chem. News*, vol. 82, p. 257.)

A table of the known properties of this family, sometimes called the Noble Gases, presumably because useless, sometimes the Bachelor Group, perhaps for a like reason, is appended.

	Helium.	Neon.	Argon.	Krypton.	Xenon.	Niton.
Quantity per 1000 by volume in the air....	0.0014	0.015	9.37	0.00005	0.000006	.....
Molecular and atomic weight.....	3.39	20.2	39.88	82.92	130.22	222.5
Boiling point.....	-267°	-233°	-186°	-152°	-109°	-154°
Melting point.....	-271°	-253°	-188°	-169°	-140°	.....

It will be noted that mention is made in the table of niton. This substance, which, along with helium, is one of the products of the decomposition of radium (*q.v.*), is like the other gases of the argon family in physical and chemical behavior, so far as has been determined. It has been investigated by Rutherford (formerly of McGill University). Further mention of it will be made when radio activity is discussed.

Attention should also be specially called to the boiling point of helium, which is about 5° absolute. The liquefaction of this gas by Onnes of Leyden in 1908 closed a chapter of events begun by Faraday in 1823 by the liquefaction of chlorine. All gases have now been liquefied and it is impossible to draw any sharp dividing line between the three states of matter, gaseous, liquid and solid. Theoretically all substances may exist in any one of the three, depending upon their temperature, pressure and individual character. Helium has recently solidified at a temperature estimated at about 2° absolute.

**The Atomic Weights of the Noble Gases.** — The observant reader will have noted that in our discussion of atomic weights we considered as the final criterion of the value "the smallest amount of an element appearing in the gram molecular weight of any of its volatile compounds" (p. 103), and the question very naturally arises as to how the atomic weight may be determined when there are no compounds. The query is briefly answered as follows:

When gases are heated the specific heat, *i.e.*, the heat required to raise a unit weight one degree centigrade, is not the same if the volume is allowed to increase as per Charles' law, as it is if



the volume is kept constant and the pressure allowed to increase. The ratio of these two specific heats, called specific heat at constant pressure  $C_p$  and at constant volume  $C_v$  is practically the same for all diatomic gases. Thus  $\frac{C_p}{C_v} = 1.41$  for hydrogen ( $H_2$ );

1.41 for nitrogen ( $N_2$ ); 1.40 for oxygen ( $O_2$ ); 1.39 for hydrogen chloride. For polyatomic gases it is a still smaller value, thus for carbon dioxide ( $CO_2$ ) it is 1.31; for ammonia ( $NH_3$ ) 1.30; for alcohol ( $C_2H_5OH$ ) 1.13, etc. For gases known to be monatomic, *i.e.*, for gases whose molecular weight and atomic weight are the same, this value is greater than 1.4, for example, mercury with an atomic and molecular weight of 200 the ratio  $\frac{C_p}{C_v} = 1.67$ . The

simplest explanation of the greater absorption of heat by gases of greater complexity when their specific heat is determined under constant pressure is that some heat goes to increase the *internal* motion of the molecules, *i.e.*, to increase the *intra* rather than the *inter* molecular motion. It is obvious that if molecules are monatomic no such intramolecular motion is possible. Since, then, the "noble gases" have a ratio of specific heats of the value approximating that of mercury, for example  $\frac{C_p}{C_v}$  for argon = 1.65, the

deduction is that argon and its fellows are monatomic. It is apparent that the reasoning is not conclusive, since if the atoms composing molecules are so closely cohesive as to resist the tendency of heat to change their respective motions no such absorption of energy would be evidenced. However, in the absence of any evidence to the contrary, we may properly assume these gases to be, like the vapor of mercury, zinc, and of many other elements at very high temperatures, monatomic. (See also Mellor, p. 564 and 836.)

**Liquid Air.**—When gases are highly compressed they fail to behave in accord with the generalization known as Boyle's Law. This is partially accounted for on the assumption that as the molecules approach more closely cohesion between the molecules begins to be exerted to an appreciable extent. Thus, as was shown by Andrews in 1869, carbon dioxide contracts more rapidly than in accord with Boyle's Law and when a certain pressure is reached the gas begins to liquefy and any further attempt to increase the pressure only results in the liquefaction of more gas until all is liquefied. At  $0^\circ$  the pressure required is but 35.4 atmospheres for

carbon dioxide. As the temperature rises the pressure required to produce liquefaction increases, until for carbon dioxide at 30° C. the pressure required is about 70 atmospheres. Above 31° however, no pressure, however great, appears to be sufficient to produce liquefaction. What occurs with carbon dioxide also occurs with all other gases at varying pressures and temperatures.

The maximum temperature at which pressure alone is sufficient to convert a gas to the liquid state is known as the critical temperature and the table below gives in column I this value for a few of the more common gases and volatile liquids. The value of the pressure required to liquefy a gas at such a temperature is known as the critical pressure, and is given in column II. It will be observed, then, that any gas, the critical temperature of which is above any readily obtained temperature, may be liquefied by pressure alone. In 1805-06, Northmore, professor of botany in Edinburgh, compressed chlorine, hydrochloric acid and sulfur dioxide into the liquid state. No developments followed, and real progress dates from 1823, when Faraday (Phil. Trans. 113, p. 189-198) conducted the first *systematic* experiments which had as a result the development of the subject. He liquefied chlorine by warming chlorine hydrate in a sealed bent tube, one end of which was immersed in ice and salt. Using the same method, he and Davy liquefied a number of gases and were unable to liquefy a number of others. In 1845 he again published a paper (Phil. Trans. 135, p. 155; see also Alembic Club Reprints, No. 12), in which he showed that by decrease of temperature and increase of pressure a long list of gases could be liquefied. A certain number not liquefiable under his conditions were called permanent gases. These were oxygen, hydrogen, nitrogen, nitric oxide, carbon monoxide and methane. (It is not to be supposed that during this interval no others were interested or that no others made progress. A full account of gas liquefaction is furnished by Hardin, Liquefaction of Gases, and by Travers, Study of Gases.)

After Andrews' work above mentioned (p. 278) it was obvious that all gases could be liquefied if only the temperature be sufficiently lowered, that is, in terms of the kinetic hypothesis, if the rate of motion of the molecules be decreased to a point when cohesion could be effective. Hence, due to the efforts of a number of investigators, the subject was developed both from the theoretical and practical standpoint until in 1877 Cailletet, in France, and Pictet, in Switzerland, independently liquefied oxygen. (Cailletet was an



iron master, Pictet a manufacturer of ice-making machines.) The principle used to secure the low temperatures required for liquefaction at reasonable pressures depends upon what is known as the "Joule-Thompson effect" of the expansion of gases from a higher to a lower pressure. In general, this results in a lowering of the temperature (for full discussion the student is referred to texts on Physical Chemistry and for a brief discussion to Mellor's *Inorganic Chemistry*, p. 124). By this means, *i.e.*, compressing the gases strongly, at low temperatures, allowing the heat so produced to escape and then permitting expansion of the gas with consequent lowering of the temperature, one gas after another was liquefied until air was liquefied in 1878. By 1884, Wroblewski and Olszewski were able to improve the apparatus required so that they were able to



FIG. 73.

announce the physical properties of liquid air, nitrogen, oxygen, carbon monoxide and methane.

In 1893, Dewar devised an apparatus which served as a suitable storage reservoir for liquid gases. This apparatus, known as the Dewar Bulb, consists of a double-walled glass vessel (see Fig. 73) with the air exhausted

from between the walls, and, frequently, the inner wall "silvered" to diminish absorption of heat. These vessels are now a common equipment of automobilists and picnic parties and are known as "thermos" bottles.

Subsequent improvements of the machinery for the process by Linde, Tripler and Hampson (see Fig. 74) have made liquid air a fairly cheap commodity of very great use in scientific advance and, about 1898 to 1900, the object of enthusiastic prophecy concerning its uses as a refrigerant, motive power and explosive. (See *Sci. Am.*, Sup. Vol. 48.) These prophecies have not yet been fulfilled.



FIG. 74.

Table of Gas Constants

	Absolute boiling point.	Absolute melting point.	Critical temp.	Critical pressure in mm.	Density at boiling point.	Color.
Water.....	373.0	273	647	152,000	1.00	Colorless
Hydrogen.....	20	16	35	11,600	0.06	Colorless
Oxygen.....	90.5	below 50	154	44,080	1.131	Bluish
Nitrogen.....	77.5	60	124	20,930	0.791	Colorless
Carbon dioxide.....	194	216	304.35	55,400	1.19	Colorless
Carbon monoxide.....	83	66	137	25,400	.....	Colorless
Nitric oxide.....	123.1	.....	179 (?)	54,000 (?)	.....	Colorless
Nitrous oxide.....	183.2	170.3	310	.....	.....	Colorless
Methane.....	108.3	.....	191	42,400	0.416	Colorless
Acetylene.....	140.5	.....	308	46,375	.....	Colorless
Fluorine.....	186	.....	419	.....	1.11	Yellowish
Chlorine.....	239.6	.....	419	70,440	1.507	Yellow
Hydrogen sulfide.....	211.5	.....	373	69,900	.....	Colorless
Ammonia.....	234.5	197.5	404	85,900	.....	Colorless
Helium.....	4.5	below 2	5	.....	.....	Colorless
Neon.....	30.40	.....	below 65	.....	.....	Colorless
Argon.....	86.90	.....	155.6	40,200	1.212	Colorless
Krypton.....	121.33	.....	210.5	41,240	2.155	Colorless
Xenon.....	163.9	.....	287.8	43,500	3.52	Colorless

**Exercises.** — 1. Is the composition of the air, so far as the two principal components are concerned, correctly represented by the formula  $N_4O$ ? Give detailed reasons for your answer.

2. Given a quantity of air, detail how each of its components may be isolated. Give reasons for considering air a mixture.

3. A sample of moist air confined over water at  $20^\circ\text{C}$ . and at 760 mm. has a volume of 20 cc. If when mixed with 25 cc. of hydrogen at the same temperature and pressure and exploded there results a total volume contraction of 12.3 cc., what is the percentage of oxygen by volume? What is the volume this oxygen would occupy when dry at  $0^\circ$  and 760 mm.?

4. If all the oxygen in the air were by union with carbon converted to carbon dioxide, what would be the percentage by volume of the latter?

5. Calculate the quantity, in liters, of the water in the form of vapor in a room  $20 \times 20 \times 10$  meters, if the humidity is 66% at  $20^\circ\text{C}$ . How many liters of liquid would precipitate if the air were cooled to  $0^\circ\text{C}$ .?

6. What is the partial pressure of oxygen in "saturated"



air (humidity 100%) at 760 mm. and  $0^{\circ}\text{C}$ ., and how much oxygen would dissolve in 100 cc. of water in contact with such air?

7. The specific gravity of liquid oxygen being 1.13, what would be the depth of the liquid oxygen layer formed on the earth were the whole quantity present in the air at normal pressure to be liquefied?

8. If a person exhales 20 liters of carbon dioxide per hour, how long would it take him to raise the carbon-dioxide content of a room,  $4 \times 4 \times 3$  meters, to 0.07%, provided no outside air were admitted?

9. The specific gravity of carbon dioxide is 1.5. Why does it fail to collect at the bottom of a badly ventilated room?

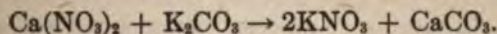
10. What volume of dry air would have to be liquefied in order to have in the liquid one liter of liquid inert gases, calculated as argon?

## CHAPTER XVI

### NITRIC ACID AND OTHER COMPOUNDS OF NITROGEN

**Occurrence.** — Nitric acid, as such, does not occur free in nature except as evanescently produced by electrical discharges and the subsequent reaction of the oxide with atmospheric moisture. Its salts are abundant and of wide distribution. There are great beds of sodium nitrate,  $\text{NaNO}_3$ , especially notable being that in northern Chile, which are said to cover an area of upwards of 150,000 square miles and are from one to ten feet thick. They consist of from 5 to 50% pure nitrate, which is hence called Chile saltpeter. Such beds can exist, of course, in only a practically rainless region.

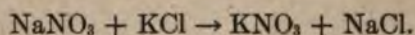
When organic nitrogenous compounds decay in the presence of calcium compounds a part of the organic nitrogen is converted, probably by bacterial agency, into calcium nitrate. In the presence of potassium salts, this is converted into the somewhat less soluble potassium nitrate. Nitrates are thus present in varying quantities in all soils. In hot and dry countries this operation results in the formation of considerable quantities of nitrates; which are found as efflorescent powders wherever sewage or other refuse is deposited. When soil so impregnated with nitrates is leached with water and treated with the extract of wood ashes,  $\text{K}_2\text{CO}_3$ , the calcium or other nitrates are changed thus:



The calcium carbonate is insoluble, and the filtrate may be concentrated to crystallization, and the crude saltpeter, sometimes known as Bengal saltpeter, may be purified by recrystallization. Formerly in certain parts of Europe artificial beds of lime and manure were prepared and leached for the preparation of nitrate, essential for the manufacture of gunpowder. These were known as niter farms or plantations. With the introduction of the East India supply, they were found unprofitable. At the present time



most of the potassium nitrate is prepared by double decomposition from Chile saltpeter and potassium chloride.

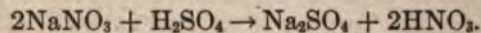


This method, in turn, promises to give way to the previously mentioned (p. 260) method of preparing nitrates from the nitrogen of the air.

Nitrates are present in most surface waters, their origin being partly due to soil leaching and partly to absorption of ammonium nitrate from the air. Ordinarily the quantity is but fractional parts per million unless with the addition of that derived from decaying animal matter. The quantity of nitrates in water is an indication of its sanitary condition.

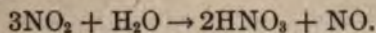
**History.** — Nitric acid was certainly known in most ancient times and the date of its discovery is unknown, but it was Lavoisier (1776) who recognized its constituents and Gay-Lussac (1816) who, considering it as an anhydride, showed its composition to be expressed by the formula  $\text{H}_2\text{O} \cdot \text{N}_2\text{O}_5$ . Since the demonstration by Graham, 1833, of the relation between water and anhydrides (see phosphoric acids) it has been usual to represent it by the formula  $\text{HNO}_3$ .

**Preparation.** — 1. Nitric acid is usually prepared from Chile saltpeter by distillation with sulfuric acid.



If the dry salt and acid are used, the pure acid obtained decomposes somewhat and the distillate is highly colored by the dissolved product of its decomposition, nitrogen peroxide. Of course, if crude niter is used the distillate will be correspondingly impure. It may be purified by redistillation with sulfuric acid, and the nitrogen peroxide may be removed by passing a current of air, or carbon dioxide, through the liquid. In this manner a nearly pure nitric acid may be had. The ordinary concentrated nitric acid is, however, purposely prepared by using diluted sulfuric acid so that the distillate may contain about 32 per cent water and have a specific gravity of 1.42, since solutions of greater concentration, as well as the pure acid, are unpleasantly unstable.

2. Nitric acid may also be made by the solution of nitrogen peroxide in water.



With the success of the Birkeland-Eyde process (*q.v.*), this method may eventually replace the method previously mentioned. (See Fig. 75.)

3. Nitric acid is also produced when ammonia is burned in oxygen and platinum is used as catalyst (*cf.* p. 265).

**Properties.** — Nitric acid is a liquid at ordinary temperatures with a boiling point of  $86^\circ$  and specific gravity of 1.56 at  $0^\circ$  C. It is very hygroscopic and fumes strongly in the air. If distilled it partially breaks down into water, oxygen and nitrogen peroxide.  $2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + \text{O}$ . The water remains in the residual acid until, with rise of the

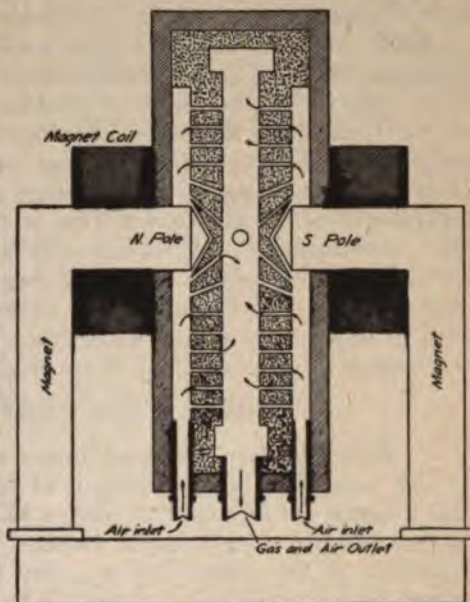


FIG. 75.

boiling point, at  $120.5^\circ$ , a mixture distills with but little decomposition. The distillate has a specific gravity of 1.414 at  $15^\circ$  C. and an acid concentration of 68 per cent. More dilute solutions when boiled lose water until the same concentration is reached. The pure acid freezes at approximately  $-55^\circ$  C., and with addition of water the freezing point falls until a cryohydric point is reached. (See Fig. 76.) Further addition



FIG. 76.

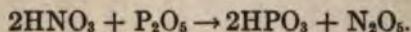
of water causes a rise in the freezing point to  $-38^\circ$ , when crystals



having the composition  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ , or  $\text{H}_3\text{NO}_4$ , form. At  $-18.2^\circ$  another crystalline hydrate,  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ , separates. It would seem that there should be a crystalline hydrate,  $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , especially as this is approximately the composition of the acid of constant boiling point. No such maximum appears in the curve. (See Küster & Kremann, *Zeit. f. Anorg. Chem.* 41, p. 1.)

Nitric acid enters into a huge variety of chemical operations, many of them of vast industrial importance (*vide* uses). All of these sorts of reaction may be reduced to four types.

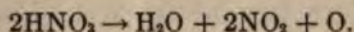
1. **Union with Water.**—The compound  $\text{HNO}_3$  reacts readily with water with evolution of heat and contraction of volume. It is a rather powerful dehydrating agent. However, the concentrated acid, 68 per cent  $\text{HNO}_3$ , is already hydrated to the extent represented by the formula  $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , and consequently the dehydrating action is only of importance when the so-called fuming nitric acid is employed. Of course more powerful dehydrating agents may extract water from the acid. Thus phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , reacts with it to produce nitrogen pentoxide:



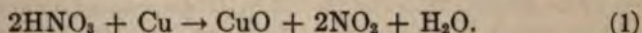
2. **Acid Action.**—The acid ionizes very readily in solution, and on the basis of its conductivity, is at normal concentration 82 per cent ionized. It is, therefore, very active as an acid. When added to metals of greater solution tension than hydrogen, *i.e.*, above hydrogen in the electromotive series (*vide* electromotive series), it is to be expected that hydrogen is formed; as is indeed the case when very dilute acid is permitted to act on certain metals, as magnesium. If, however, we compare this statement with the following paragraph it will be observed that only under special circumstances will the hydrogen so obtained be actually liberated. It is not reasonable however, to assume the displacement of hydrogen and its subsequent oxidation when metals of lesser solution tension than hydrogen are employed (as is done by so many writers of texts). Similarly, when salts are treated with nitric acid metathesis should occur, but whether the other acids so liberated can be obtained is dependent upon their nature, *i.e.*, whether easily volatilized, precipitated or oxidized. With sulfides, of course, no hydrogen sulfide is to be expected, since it is so readily oxidized.

3. **Oxidizing Action.**—Nitric acid finds its most characteristic applications because of the ease with which it suffers reduction. This is illustrated by its behavior with metals, which are lower in

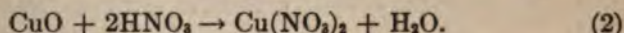
the electromotive series than hydrogen, with carbon, starch, sugar, etc. The degree of reduction depends in part on the power of the reducing agent and in part on the concentration of the acid. Primarily, however, we may consider the reaction to be of the following type:



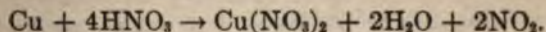
This reaction does not go far in the direction indicated unless the oxygen formed is consumed by a suitable substance. Thus,



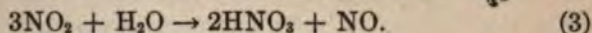
What happens subsequently, depends of course upon the nature of the oxide produced. In this case, the oxide reacts with the acid as indicated:



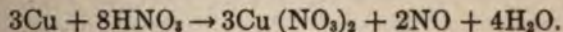
Adding (1) and (2) we have:



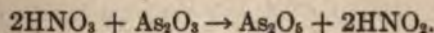
In case we have dilute acid, it appears that nitrogen peroxide is decomposed by the water as indicated by the reaction:



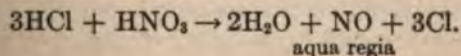
The nitric acid so formed is, of course, available for continuing the action. We have, then, with dilute nitric acid by addition of equations (1), (2) and (3):



It will be seen, also, that nitrogen peroxide,  $\text{NO}_2$ , is capable of reduction, so that a mixture of nitric oxide,  $\text{NO}$ , and peroxide,  $\text{NO}_2$ , is formed under some circumstances. These substances unite ( $\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$ ). This latter oxide, which exists only in solution or in liquid form, is the anhydride of nitrous acid (*q.v.*). We may have, then, with proper concentration of nitric acid and character of reducing agent, nitrogen peroxide, nitrous anhydride or nitric oxide. With arsenic trioxide, for example, the reaction may run:



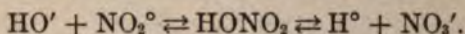
With hydrochloric acid we have:



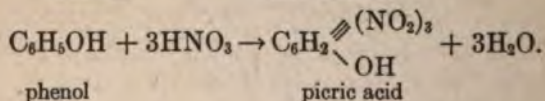
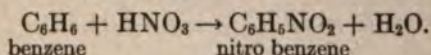


4. **Nitro-forming Action.**—The mode of behavior of nitric acid which is most extensively employed practically is that which can be most clearly outlined in the light of the structure of the acid. If we accept the structure most reasonable in the light of the behavior of the acid we may indicate it as follows:  $\text{H}-\text{O}-\text{N} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$

By this formula we intend to indicate the presence in the concentrated acid of one hydroxyl group and a valence of the nitrogen of five. In the presence of water the prevailing activity of the acid is due either to hydrogen ions, or to the ease of reduction of the valence of the nitrogen, but it is quite possible that the nitric acid may be amphoteric, as indicated by the equilibrium formula:

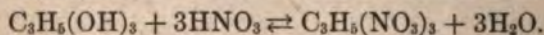


And in the absence, or near absence, of water the suppression of the hydrogen ion enables the other tendency to manifest itself. At any rate, with substances not basic, but readily subject to loss of hydrogen, we have such reactions as:



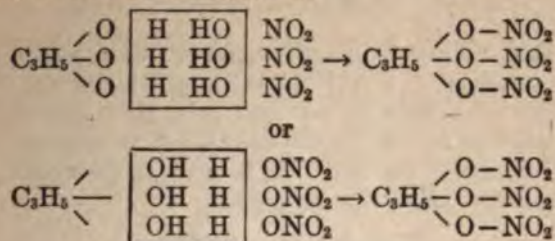
These and similar reactions are accomplished by splitting off the hydroxyl group from the acid. Such "nitro-compounds" are of frequent formation when nitric acid acts upon organic compounds. One of these, xanthoproteic acid, is formed when nitric acid acts upon the skin. These reactions take place best in the absence of water, and hence are carried out by addition of concentrated sulfuric acid, which unites with the water as indicated upon p. 237.

A very important group of reactions accomplished by nitric acid may perhaps be classed either as of type 2 or 4. These are those with alcohols. Alcohols are usually considered as neither basic nor acid, but contain the hydroxyl group. A familiar example is glycerine  $\text{C}_3\text{H}_5(\text{OH})_3$ . With nitric acid it reacts as follows:

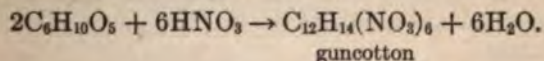


Here again the presence of concentrated sulfuric acid assists the completion of the reaction by removal of water. On the assump-

tion that the substance is a nitro body it is called nitroglycerine. In view of the fact that the same body is produced whether the nitric yields the hydroxyl or hydrogen radical, it, nevertheless, is a true nitrate, whether the reaction is:



Similar reaction is produced between alcohol-like substances, such as wood fiber or cotton fiber (cellulose).



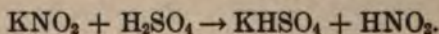
Nitrates of this latter type containing 2, 3 or 4 nitrate radicals are used when dissolved in ether to make collodion, or artificial skin, and smokeless powders, and mixed with camphor to make celluloid. These nitrates differ from metallic nitrates in being usually insoluble in water, and even if soluble they do not ionize to furnish nitrate ions.

**Uses.**—It will have been observed that nitric acid is used for a large variety of purposes, especially where its oxidizing or its nitro-forming properties may be turned to account. It finds, therefore, a variety of applications in the laboratories and in the manufacture of nitroglycerine, guncotton, picric acid, trinitrotoluene, fulminates and other explosives, and, the still somewhat dangerous collodion and celluloid. The salts of the acid, the nitrates, are also manufactured for use as fertilizers, in the preparation of black powder and in the manufacture of pyrotechnics.

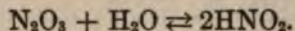
**Nitrous Acid and Nitrous Anhydride.**—If nitrates of the alkali metals are heated to a sufficiently high temperature oxygen is liberated, as has already been mentioned. This reaction takes place the more readily if an oxidizable substance is present. Thus, if lead is heated with potassium nitrate we have  $\text{KNO}_3 + \text{Pb} \rightarrow \text{PbO} + \text{KNO}_2$ . The latter product is a salt of nitrous acid



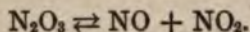
and may be dissolved and purified by recrystallization. When we treat nitrites so prepared with non-volatile acids we should naturally expect to obtain nitrous acid by double decomposition:



While the acid undoubtedly is formed, if we attempt to obtain it in pure condition by distillation reddish brown fumes are formed, which, if cooled by ice and salt, give us a blue liquid, which decomposes before its boiling point is reached. This is apparently nitrous anhydride,  $\text{N}_2\text{O}_3$ , and if dissolved in water forms the reversible equilibrium system,

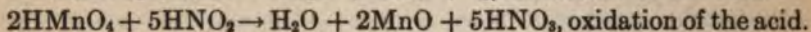
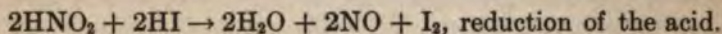


If the solution is treated with a base, nitrites are formed. When we attempt to volatilize the blue compound and determine its molecular weight it dissociates into the two gases, nitric oxide and nitrogen peroxide.

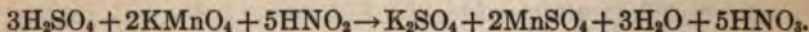


Apparently its composition in solution is expressed by the formula  $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$ , and that of the acid by  $\text{HO}-\text{N}=\text{O}$ , in both of which the nitrogen is trivalent.

† Nitrous acid solutions are both readily reduced and readily oxidized, and hence are capable of effecting a variety of reactions which are extremely convenient. These may be illustrated:



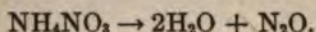
The latter reaction is usually carried out, using permanganates with sulfuric acid, and may be expressed:



Nitrites find a variety of applications in the laboratory and the arts, in particular being extensively used in the manufacture of dyes.

**Oxides of Nitrogen.**—Incidental mention has already been made of nitric oxide and nitrogen peroxide and it is now in order to formally discuss these oxides as well as another one even more interesting. Nitrous and nitric anhydrides have been mentioned.

**Nitrous Oxide.**— This substance was first prepared by Priestley (1772) by reduction of nitric oxide by means of moist iron filings, and by some curious freak of imagination was supposed to be extremely poisonous, being considered the "very principle of contagion." The bravery of young Humphry Davy (see "Sir Humphry Davy, Poet and Philosopher") was therefore great when, in 1794, through inhalation he discovered its peculiar anæsthetic properties, which made it for a long time a popular plaything and gave to it the name of laughing gas. For many years it was used, with admixed oxygen, as an anæsthetic in mild surgical operations. Its place as an anæsthetic is now usurped largely by other substances, particularly by ethyl chloride ( $C_2H_5Cl$ ). The most convenient method of its manufacture is to heat ammonium nitrate, which decomposes as indicated:



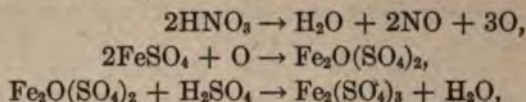
It is also formed, mixed with other oxides and nitrogen, when sufficiently dilute nitric acid acts upon tin or zinc. The gas is an endothermal compound and decomposes with the liberation of 18,000 cal. per gram molecule. It is, therefore, unstable and will support combustion almost as readily as free oxygen and more readily than air, in which, of course, oxygen is but  $\frac{1}{5}$  of the total gaseous concentration. It will not yield its oxygen to nitric oxide and is hence readily distinguished from free oxygen.

The gas may be converted into its elements either by heating or by detonation with a fulminating cap. It is fairly soluble in water, 130 volumes to 100 at  $0^\circ$ , and hence is more conveniently collected over warm water, in which it is practically insoluble. No apparent reaction between it and water takes place, though it might be expected to form hyponitrous acid. The latter is formed by the reaction between hydroxylamine and nitrous acid as indicated,  $NH_2OH + HNO_2 \rightarrow 2HNO + H_2O$ , and the acid, which is very weak, decomposes on warming into hyponitrous anhydride and water. The action is apparently not readily reversible. The acid is dibasic and has the probable composition  $H_2N_2O_2$ .

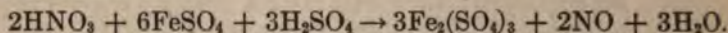
**Nitric Oxide** is, as has been mentioned, formed by the action of dilute nitric acid on reducing substances. It is thus formed in a variety of reactions. Perhaps the most convenient method of preparing it free from admixed oxides of nitrogen is to add nitric



acid to a solution of ferrous sulphate and sulphuric acid. The reactions which take place may be indicated:



and by addition,



The gas is colorless and difficultly liquefiable, b.p.  $-142^\circ \text{C}.$ , and is but slightly soluble in water. It is endothermic and explodes when it is detonated, yet it is the most stable of the oxides of nitrogen. It decomposes reversibly when heated and the point of equilibrium at various temperatures is indicated by the following table taken from Nernst (*Zeit. für Anorg. Chem.* 49, p. 213).

Temperature, absolute.	Calculated per- centage, NO.	Found percentage, NO.
1811	0.35	0.37
2195	0.98	0.97
2675	2.37	2.23
3200	4.43	5

This reaction is given special mention for these reasons: It illustrates Le Chatelier's law (*q.v.*) in that while the reaction involves no change of volume,  $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$ , yet the formation of the gas at higher temperatures tends to reduce the stress by reason of absorption of heat. Also it seems to illustrate the reason that the synthetic formation of nitrates, of which the first step is the formation of this oxide, takes place only at the higher temperature of the electric arc. It also is interesting as illustrating the change of speed of reactions with change of temperature. For it appears that while at the temperature about that indicated in the first column, it takes about five seconds for equilibrium to be reached whether one starts with nitric oxide or air. Yet at  $750^\circ$ , the time required is about 800 years, and at room temperature almost infinitely longer. Nitric oxide then, if formed at high temperature and suddenly cooled, is stable at ordinary temperatures.

Nitric oxide is capable of a variety of reactions, which may be classed as oxidizing, reducing and additive. As an oxidizing agent

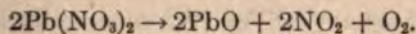
it is not vigorous, but with moist iron, and other metals also, it is reduced to nitrous oxide. It will also support the combustion of substances which ignite at low temperatures, thus if burning phosphorus be lowered into a jar of the gas it continues to burn vigorously. Burning wood and other combustible materials are quenched by the gas. Carbon disulfide vapor mixed with the gas and ignited produces a brilliant flash of light rich in actinic light (p. 441). The gas functions as a reducing agent in readily uniting spontaneously by oxygen to form nitrogen peroxide. Yet it is not combustible in the ordinary sense, and its union with oxygen is not accompanied with a change of temperature (?). The most characteristic mode of behavior is best explained by reference to its structural formula, which in view of the molecular weight of the gas, 30, can scarcely be other than  $N=O$ . The nitrogen is then bivalent, while nitrogen normally manifests a valency of three or five. The oxide may then be considered as unsaturated and hence unites readily with other unsaturated compounds. Chemical union of this type is frequently spoken of as *molecular* and the compounds are classed as *molecular compounds*. Thus with ferrous sulfate nitric oxide forms in solution an unstable compound, which may perhaps be

considered to have the formula  $Fe \begin{smallmatrix} NO \\ \diagdown \\ SO_4 \end{smallmatrix}$ . We have also in aqua regia

the unstable compound  $NOCl$ , and with fluorine the compound  $NOF$ . Substances of this type are called "nitrosyl" compounds. The molecular compounds, of which the nitrosyl compounds are examples, are very numerous and include such compounds as the crystalline hydrates as  $CaCl_2 \cdot 6H_2O$ . The double salts, as ferrous ammonium sulfate,  $(NH_4)_2SO_4 \cdot FeSO_4$ , etc. There seems to be no particular value in the classification except that frequently the valence relations of the elements, *i.e.*, the structural formulæ, are not readily arrived at without making more or less unwarranted assumptions. There is no warrant in fact, however, for assuming that the combining relations are different from those in less complex compounds.

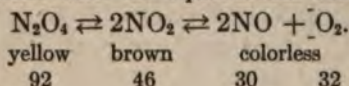
**Nitrogen Peroxide.**—When the nitrates of heavy metals are heated instead of the sort of decomposition which takes place with ammonium nitrate (p. 231), or with alkali nitrates (p. 230), the products of the reaction are the oxide of the metal, oxygen and a gas which according to the temperature seems to be either  $NO_2$  or  $N_2O_4$ .

For example:



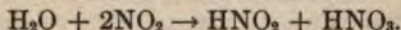


The gas is also formed when nitric oxide and air are brought into contact,  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ , and when concentrated nitric acid is brought into contact with metals or other reducing agents. The gas is reddish brown to yellow, depending upon the temperature, and has a molecular weight, which varies between 45.7 at  $154^\circ$  and 76.7 at  $27^\circ$ . The depression of the freezing point of a solution of the gas corresponds to a molecular weight of 92. When the temperature is raised above  $154^\circ$  the color and density continue to diminish and finally the density corresponds to a molecular weight, which is the mean of those of oxygen and nitric oxide. These changes reverse themselves on cooling. It would seem that we have here to deal with an equilibrium reaction as indicated:

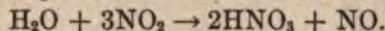


The gas is readily condensed to a yellow liquid at low temperatures and the liquid boils at  $26^\circ \text{C.}$ , but at lower temperatures has a high vapor tension. Its melting point is  $-9^\circ$ , and the crystals are colorless.

Nitrogen peroxide is poisonous and inhalation of even small amounts produces headache and nausea. It supports combustion of any substances which unite vigorously with oxygen. It is, as may be inferred from the above, a vigorous oxidizing agent. Thus it oxidizes phosphorus, potassium, etc. It liberates iodine from iodides and in general acts as a powerful oxidizing agent should. The special vigor of "fuming" nitric acid is due to the presence of this substance in solution. Yet the gas may itself be oxidized rather readily to nitric acid by powerful reagents, such as permanganic acid. The most interesting reaction of nitrogen peroxide is that with water. If the temperature is kept low it dissolves, forming a mixture of nitric and nitrous acids.



If, however, the temperature is that of the room or above we have:



This reaction is that which accounts for the conversion by it of solutions of bases into nitrates. It also explains the apparent difference between the behavior of dilute and concentrated nitric acid as oxidizing agents, while in reality the action is the same. This reaction, combined with that of its formation from nitric oxide and oxygen, has an interesting historical aspect, since Priestley

devised a method of determining the "goodness of air," *i.e.*, its oxygen content, by admitting to a measured volume of air, enclosed above water or an alkaline solution, measured volumes of nitric oxide. The peroxide formed is dissolved and the maximum diminution of volume is a measure of the oxygen present. The instrument Priestley used is our present eudiometer ( $\xi$  = goodness,  $\mu\eta\rho\omicron\nu$  = measure). (Fig. 77.) Nitrogen peroxide as the dioxide can scarcely have any other formula than that represented

by the graph  $\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$  and consequently, since

nitrogen usually manifests a valency of three or five, it is to be expected that, like nitric oxide, it might also satisfy itself by formation of molecular compounds by addition. An interesting case is its union with copper to form copper nitroxyl,  $\text{Cu}(\text{NO}_2)$ . The  $\text{NO}_2$  thus behaves as a univalent radical.

This reaction perhaps explains the catalytic effect of oxides of nitrogen in hastening the action of nitric acid on copper and other metals, though just why shaking the metal slows up the reaction, which it does, is *not* apparent.

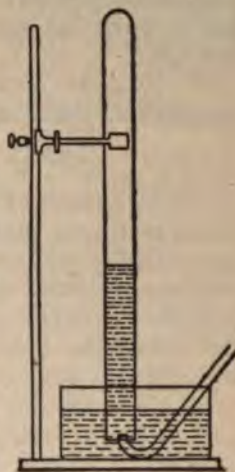
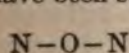


FIG. 77.

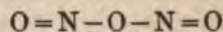
**Structural Formulæ of Nitrogen Compounds.** — While in the preceding pages we have of necessity discussed the structural formulæ of these compounds, a résumé may be advantageous. No attempt will be made to give the reasons leading to the graphs presented nor a discussion of alternative graphs which may be or have been suggested.



nitrous oxide



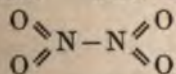
nitric oxide



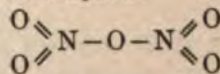
nitrous anhydride



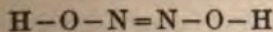
nitrogen dioxide



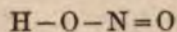
nitrogen tetroxide



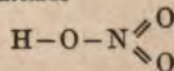
nitrogen pentoxide



hyponitrous acid



nitrous acid

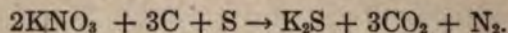


nitric acid



**Exercises.** — 1. If the equation representing the decomposition of nitroglycerine is:  $4\text{C}_3\text{H}_5(\text{NO}_3)_3 \rightarrow 12\text{CO}_2 + 10\text{H}_2\text{O} + 6\text{N}_2 + \text{O}_2$ , what volume of gas would be produced from a formula weight in grams when the gaseous products are measured at  $100^\circ\text{C}$ . and 760 mm.?

2. What is the volume of gaseous products from 227 grams of gunpowder measured at  $100^\circ$  and 760 mm. if the reaction is:



3. Make correct equations representing the following reactions. Nitric acid and phosphorus pentoxide producing metaphosphoric acid,  $\text{HPO}_3$ , and nitrogen pentoxide. Nitric acid and sulfur producing sulfuric acid and nitric oxide. Nitric acid and sulfur producing sulfuric acid and nitrogen dioxide. Nitric acid and zinc producing zinc nitrate, nitric oxide and water. Nitric acid and cellulose producing trinitrocellulose and water.

4. Give all the details required for the preparation of pure sodium nitrite from impure sodium nitrate.

5. If nitrogen trioxide,  $\text{N}_2\text{O}_3$ , dissociates completely into nitric oxide and nitrogen dioxide, what is the weight of the gram-molecular volume?

6. Collect from the text all the facts tending to show that in the liquid form the blue compound is nitrous anhydride  $\text{N}_2\text{O}_2$ .

7. Show by equations that nitric oxide is both an oxidizing and reducing agent.

8. If the gram-molecular volume of the mixture of nitrogen dioxide and nitrogen tetroxide at  $10^\circ$  weighs 80 grams, what is the percentage amount of each compound present?

9. If nitrogen peroxide is dissolved in cold water the products are nitrous acid and nitric acid. Formulate the equation. What other oxide reacts in an analogous manner.

10. If you had a mixture of nitrous oxide, oxygen and nitrogen, how could you determine the presence of each gas? How would you undertake to estimate the quantity of each component of the mixture?

## CHAPTER XVII

### PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

**Occurrence.**—Phosphorus never occurs free, but in the form of compounds is of wide distribution in small quantities. It also occurs in large mineral deposits. The commonest natural forms are modifications of calcium phosphate; of which great deposits occur in Florida, South Carolina, Tennessee, Montana, Utah, Wyoming and in Ontario, Canada. The two mineral forms are phosphorite,  $\text{Ca}_3(\text{PO}_4)_2$ , or phosphate rock, and fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{CaF}_2$ . Considerable quantities occur also as vivianite,  $\text{Fe}_3(\text{PO}_4)_2$ .

Phosphates occur in all soils and are essential to soil fertility. Plants consume the mineral phosphates and from the plants the animals obtain the needed material to build bones, which are approximately 40 per cent calcium phosphate, and organic phosphates, of which the most important is nuclein. In consequence of the utilization of phosphorus compounds by the animal organisms, phosphates are present in the dejecta of animals and certain fossil forms of these are known as coprolites. In the urine of mammals phosphates are present and this was the first source of the manufacture of the element.

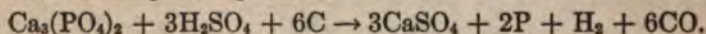
**History.**—Phosphorus is supposed to have been discovered by Brand, an alchemist, in 1668 by distilling the residue of evaporated urine. The striking phenomenon which accompanies its exposure to air in the dark, the faint luminosity produced, gave to the substance the name (from  $\phi\omega\varsigma$  = light,  $\phi\acute{\epsilon}\rho\epsilon\upsilon\alpha$  = to bear,  $\phi\omega\varsigma\phi\acute{\epsilon}\rho\omicron\varsigma$  = Lucifer, the morning star). The recognition of the substance as an element we owe to Lavoisier.

**Phosphorescence.**—There are three, at least, distinct kinds of luminosity produced at ordinary temperatures which are known as phosphorescence. One of these is the glow produced by the phosphorus itself, which is due to the liberation of energy in the form of light during the oxidation of the element. There are ap-

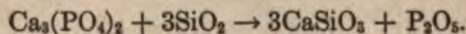


parently many organisms, such as the firefly, glowworm and smaller organisms which secrete a substance which, on exposure to air, oxidizes similarly with energy evolution in the form of light rather than of heat. This is sometimes called cold light and the element, phosphorus, is not involved. This variety of oxidation accounts for the phosphorescence of the sea in summer, of fox fire and of the luminosity of foodstuffs, which so often gives concern to the housewife. The third variety of phosphorescence is manifested by such substances as calcium and other sulfides, cobalt phosphate, etc., and appears to be due to the effect of intense light which sets up a motion of the molecules such that when placed into the dark this molecular motion is able to initiate ether waves. At any rate, these substances, after exposure to light, will continue to give off light for greater or lesser periods of time. These materials form the basis of "luminous paints," "miracle pictures," etc. All substances are said to be phosphorescent, in this sense, at the temperature of liquid air.

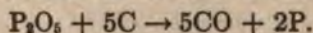
**Preparation.** — When phosphates are treated with acids, phosphoric acid is formed, *e.g.*,  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{CaSO}_4 + 2\text{H}_3\text{PO}_4$ . If phosphoric acid be sufficiently heated it breaks down into metaphosphoric acid and water:  $\text{H}_3\text{PO}_4 \rightarrow \text{HPO}_3 + \text{H}_2\text{O}$  (see phosphoric acid). If metaphosphoric acid is heated with a strong reducing agent the element is liberated: *e.g.*,  $2\text{HPO}_3 + 6\text{C} \rightarrow 6\text{CO} + 2\text{P} + \text{H}_2$ . All these operations may be carried out in one vessel; thus if bone ash be mixed with sawdust and sulfuric acid and distilled the phosphorus, which volatilizes, may be condensed and collected under water and molded into the familiar yellow sticks, in which form it usually appears on the market. The reaction may be expressed:



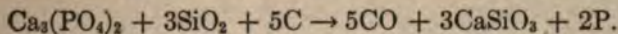
In recent years the development of the electric furnace has made possible a more economical method, which consists essentially in displacing the anhydride of phosphoric acid by the anhydride of silicic acid.



This operation requires a rather high temperature, which is furnished by the electric arc. The operation is not an electrolytic one. If the anhydride be heated with carbon it is reduced:



These two reactions may be carried out in one operation if sand, bone ash and carbon be heated in an electric furnace and the vapor of phosphorus condensed by a suitable apparatus. (Fig. 78.)



Of course, the crude phosphorus so obtained must be purified. This is done by various methods, which are trade secrets, but all consist essentially of redistilling with purifying agents, and collecting the product under water.

#### *Allotropic Modifications.*—

While in the methods described above the product is always the same, and is known as yellow phosphorus, there is at least one other well-known modification, called red phosphorus, which is obtained by heating the yellow material to 250° C. in the presence of an inert gas, or in the absence of any other material, *i.e.*, in vacuo. This change may also be produced by "sparking" the material electrically. If yellow phosphorus is allowed to

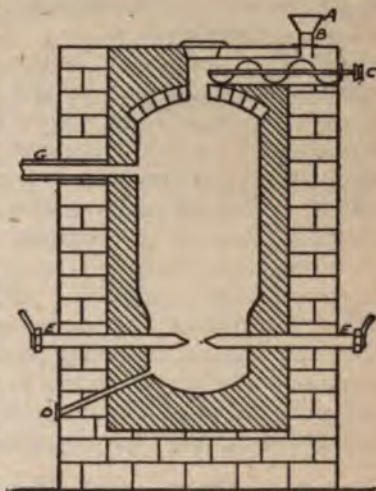


FIG. 78.

stand in the sunlight, it slowly transforms itself into the red modification. The speed of the reaction may be greatly facilitated by the presence of a catalytic agent, such as traces of iodine. If the red variety be heated until it volatilizes and the vapor quickly cooled, the product is the yellow variety. It is apparent that the red phosphorus is the more stable form and that the yellow phosphorus is only obtained because of the slow rate of the change from the metastable to the stable condition.

There are several other modifications, or allotropic forms of phosphorus which have been reported, such as black phosphorus, scarlet phosphorus, etc., but it is impossible to say definitely if they are real individual forms or not.

**Properties.**—The contrast between the physical and chemical properties of yellow and of red phosphorus is more marked than



between many different elements, yet when either variety is used to produce a given reaction, there is no difference in the resulting product, and each variety may be converted into the other without gain or loss of weight. It is not, however, to be understood that the energy relations are the same. In general, the transformation of the yellow to red variety is accompanied by the evolution of 4,000 calories of energy and, therefore, combustion, or other reaction of the varieties are accompanied by differences of energy relations of corresponding value.

Whether phosphorus vapor be derived from the yellow or red variety, the molecular weight is approximately 124. Since the atomic weight is 31 as shown by the analysis of the phosphate,  $\text{Ag}_3\text{PO}_4$  and by the molecular weight of its volatile compounds, its molecular complexity is four,  $\text{P}_4$ . In solution in carbon disulfide, yellow phosphorus also shows a freezing point depression corresponding to the formula  $\text{P}_4$ . At higher temperatures the molecular complexity falls until at about  $1700^\circ$  it appears to correspond to the formula  $\text{P}_2$ . What the character of the molecule of red phosphorus is, is unknown, since no solutions of it, suitable either for freezing or boiling point determinations are known. The cause of the wide divergence in the properties of the two varieties is then unknown. The properties in question may be conveniently contrasted by the "deadly parallel" of the printer.

Property	Red phosphorus	Yellow phosphorus
Color	Red to chocolate	Yellow to colorless
Crystalline form	Rhombohedral	Cubical
Boiling point	Nil	$270^\circ$
Melting point	(Under pressure) 500- 600°	$44^\circ$
Solubility in water	Nil	Nil
Odor	Nil	Garlic
Appearance in dark when exposed to air	No phosphorescence	Phosphorescent
Specific gravity	2.106-2.14	1.83-1.85
Specific heat	0.170	0.189
Physiological action	Non-poisonous	Poisonous
Ignition point in air	$260^\circ$	$30^\circ$
Action on chlorine	Burns if heated	Takes fire spontaneously

**Uses.**—Phosphorus, in the elementary form, is used in the manufacture of matches (see below). Since it is a virulent poison, in yellow form, and mixes readily with foodstuffs, it is frequently

used as a vermifuge (bug and rat poisons, etc). It is also used as a poison, both for purposes of suicide and murder. A solution of yellow phosphorus in carbon disulfide is used for incendiary purposes, under the name "Pettibones dope." On account of the use found in the chemical laboratory for the reactions of which phosphorus is capable, considerable quantities are so consumed. For most purposes the red variety is as well suited and much safer than the yellow. Since yellow phosphorus unites readily with oxygen at the ordinary temperature, it is frequently used to determine the quantity of free oxygen in a mixture of gases, as in air analysis. (Note: It ought to be mentioned that pure oxygen is not attacked at room temperature by yellow phosphorus. This is interesting as being contrary to the experience that reaction rates are increased by increased concentrations: cause unknown.)

Phosphorus is also used in making a variety of substances, such as the phosphorus chlorides, iodides, etc. (*q.v.*).

**Matches.**—By far the most extensive use of phosphorus is in the preparation of matches. These are of two types: the so-called "friction" match and the safety match. In general, a match head contains some readily combustible material, such as sulfur, sugar, glue, antimony sulfide, etc., in sufficiently large quantity so that its combustion may raise to the kindling point the material of which the "stick" of the match is made. In order to facilitate the combustion, the head also contains some good oxidizing agent, such as potassium nitrate, potassium chlorate, etc. In general such a mixture, while it burns readily if ignited, requires a higher kindling point than can be readily reached by friction alone. To this end is, therefore, added some yellow phosphorus or phosphorus "sesquisulfide," either of which by simple friction may be readily heated to ignition. In the safety match red phosphorus is placed, mixed with sand, on the side of the box. The rough surface, when rubbed with the match, is locally heated to a point where ignition results, but the poorly conducting sand keeps the combustion from spreading through the phosphorus on the box. Formerly only yellow phosphorus was used in match manufacture, but the matches so made are somewhat dangerous by reason of their ready ignition, also because children, and sometimes adults, by accident or intent, ate match heads. Since one match contained enough phosphorus to cause serious symptoms and as few as three have been known to cause death, the danger was not small. Above all, the manu-

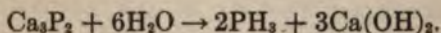


facture of these matches could not be, or at least was not, carried on without contact between the workmen and the vapors of the molten phosphorus. The result of this contact for any length of time was necrosis of teeth and bones, especially of the nose and jaw (*fossy jaw*). Recently most civilized peoples have forbidden the use of yellow phosphorus in matches. Its place has been taken by the almost as readily ignited phosphorus sesquisulfide,  $P_4S_3$ , which can be manufactured without danger to the workmen and which is much less poisonous than the yellow phosphorus.

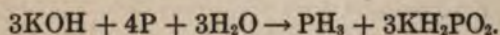
There is a very great range of formulæ suitable for match making and for information of a general character the reader is referred to the *Encyclopedia Britannica*.

**Phosphine and Other Hydrogen Compounds.** — Phosphorus forms with hydrogen a series of hydrogen compounds similar to those of nitrogen, but which show some points of striking contrast. These are: Phosphine,  $PH_3$ ; liquid hydrogen phosphide,  $P_2H_4$ , corresponding to hydrazine, and a solid phosphide,  $P_{12}H_4$ . Of these only the first will be here discussed.

If calcium phosphide is treated with water, phosphine is evolved by the reaction:



Also, if yellow phosphorus is heated with caustic potash solution the following reaction takes place:



Potassium hypophosphite

If the air above the solution be displaced by a gas which does not react with phosphine, such as coal gas, hydrogen or carbon dioxide, the gas, which as it is evolved is spontaneously inflammable, may be allowed to escape in separate bubbles through water when, as each one takes fire, a smoke ring is formed. (See Fig. 79.) If collected over water, phosphine is a colorless gas with a peculiar fishy odor. It is solid at  $-133^\circ$  and liquid at  $-85^\circ$ . Its kindling point is at about  $100^\circ$  and its spontaneous inflammability as prepared is probably due to the presence of traces of the liquid phosphine. The products of its combustion are, of course, phosphorus pentoxide and water, the former causing the smoke rings above mentioned. It decomposes when heated or when exposed to strong light into phosphorus and hydrogen. As its collection over water

would indicate, it is strikingly less soluble than ammonia; only 11 volumes per 100. Moreover, the aqueous solution is not alkaline. The gas does unite directly with strong acids to form phosphonium salts, *e.g.*,  $\text{PH}_3 + \text{HCl} \rightarrow \text{PH}_4\text{Cl}$ . These are chiefly interesting as demonstrating the relation between phosphine and ammonia.

**Oxides and Acids of Phosphorus.**—There are three oxides of phosphorus, the trioxide,  $\text{P}_2\text{O}_3$ ;

the pentoxide,  $\text{P}_2\text{O}_5$ , and the tetroxide,  $\text{P}_2\text{O}_4$ . The last mentioned corresponds to nitrogen tetroxide and is formed by heating the trioxide,  $\text{P}_2\text{O}_3 \rightarrow \text{P}_2\text{O}_4 + \text{O}_2$ , in a sealed tube at  $440^\circ$ . It decomposes water, forming phosphorous and phosphoric acids (*cf.* p. 196). No further mention will be made of it.

The pentoxide is formed when either red or yellow phosphorus is burned with free access of air. It is a white powder which sublimes slowly at  $50^\circ$ . Its vapor density, even at  $1400^\circ$ , corresponds to the formula  $\text{P}_4\text{O}_{10}$ , but ordinarily the smaller formula  $\text{P}_2\text{O}_5$  is used to describe its reactions. If heated rapidly, it melts and on cooling solidifies to a vitreous mass. It is extremely hygroscopic and is the material generally employed in drying gases for complete removal of water.

It unites with water with evolution of from 29,000 to 41,000 cal. of heat at "infinite dilution," according to whether the crystalline, amorphous or vitreous form is dissolved. Its avidity for water, coupled with the non-volatility of the corresponding acid, is so great that it may be used to liberate even the anhydrides of sulfuric and nitric acids. When the oxide is added to water without heating or when it is exposed to air, a viscous jelly-like substance is produced, which is known as **metaphosphoric acid**. This acid or its salts may be prepared in a variety of ways. It has the composition  $\text{HPO}_3$  and corresponds to the ordinary form of nitric acid. It is frequently called "glacial phosphoric acid."

When the glacial variety is dissolved in water and allowed to

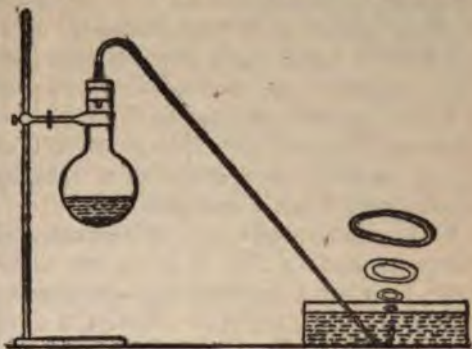


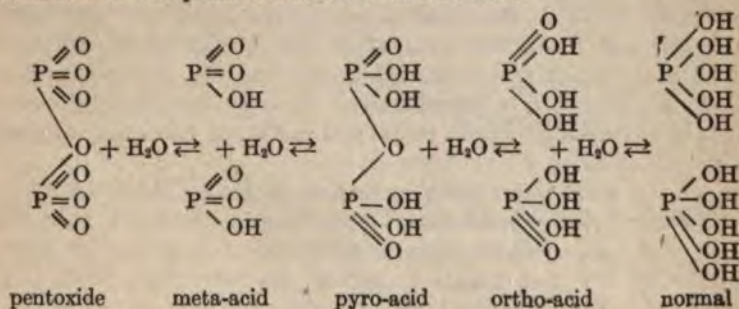
FIG. 79.



stand, it slowly changes by addition of water, or rapidly if boiled, forming the ordinary or orthophosphoric acid,  $\text{HPO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4$ , which may be obtained in the dry form by concentration in vacuo. It melts at  $38^\circ$ . It is usually marketed in the form of a thick syrup of a concentration of about 85 per cent. Being tribasic, it forms three series of salts, which are distinguished from each other by the terms primary, secondary and tertiary. Thus, primary sodium phosphate is  $\text{NaH}_2\text{PO}_4$ , secondary,  $\text{Na}_2\text{HPO}_4$  and tertiary,  $\text{Na}_3\text{PO}_4$ . It will be noted that only the last is a neutral salt. Since, however, it is a salt of a weak acid and a strong base, it is strongly alkaline in solution.

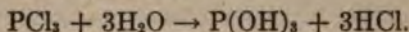
Phosphoric acid is a comparatively weak acid (see p. 175). When heated to  $250^\circ$  it loses one molecule of water from two of acid, forming a well-defined intermediate product known as *pyrophosphoric acid*,  $\text{H}_4\text{P}_2\text{O}_7$ . The salts of this acid are readily formed by heating secondary phosphates, *e.g.*,  $2\text{Na}_2\text{HPO}_4 \rightarrow \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$ .

When phosphorus pentachloride is treated with water, hydrolysis takes place and when the attempt is made to isolate the products orthophosphoric acid is obtained. Yet the interchange can scarcely be other than  $\text{PCl}_5 + 5\text{H}_2\text{O} \rightarrow \text{P}(\text{OH})_5 + 5\text{HCl}$ . The compound  $\text{P}(\text{OH})_5$ , when it exists evanescently, if at all, is known as *normal phosphoric acid*. These relations may be made clear by a consideration of the probable structural formulæ.

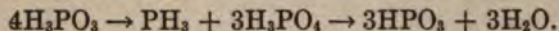


This series is so remarkable and the transformations of one variety into another, either as salt or in the free form, so valuable that a careful study of the relation expressed is advised. The relation of water to the acids is also important historically, since in a paper on the salts of these acids and the corresponding ones of arsenic, in 1833, Graham (see Alembic Club Reprints, No. 10) showed the relation between anhydrides and acids and that the

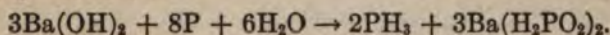
$P_2O_3$ , is usually employed. The phosphorous acid is readily formed by hydrolysis of the trichloride:



The acid so produced is, like phosphoric acid, tribasic, but, like all polybasic acids, is stronger as a monobasic acid, *i.e.*, the second and third stages of ionization take place less readily than the first. When heated the acid loses water, forming a meta-acid,  $P(OH)_3 \rightarrow H_2O + HPO_3$ , which corresponds to nitrous acid. When phosphites or phosphorous acid are heated they act like sulfites, simultaneous oxidation and reduction taking place (*cf.* sulfites and hypochlorites).



**Hypophosphorous Acid.** — When phosphorus is heated with bases simultaneous formation of a salt of hypophosphorous acid and phosphine results.

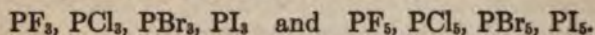


When this salt in solution is treated with dilute sulfuric acid, the free acid,  $H_3PO_2$ , remains in solution, while barium sulfate is

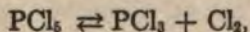
precipitated. The supposed structure of the acid is  $O=P \begin{matrix} \nearrow H \\ \text{---} H \\ \searrow OH \end{matrix}$

since only primary salts are known. The salts of this acid are used medicinally as "nerve tonics."

**Other Compounds of Phosphorus.** — The halides of phosphorus possess a special interest because of the part they play in the preparation of organic compounds and have played in the unraveling of the structure of both organic and inorganic compounds. There are two series:



The latter compounds dissociate reversibly on heating, *e.g.*:



and the explanation of this type of reaction had an important bearing on the general acceptance of Avogadro's hypothesis and its consequent effect on the systematic development of chemistry. The importance of these compounds in organic chemistry is due



to the fact that they are hydrolyzed not only by water, as was illustrated in the preparation of hydrochloric and hydrobromic acids (*q.v.*), but also by any substance containing an hydroxyl group. Thus  $\text{PCl}_3 + 3\text{C}_2\text{H}_5\text{OH} \rightarrow \text{P}(\text{OH})_3 + 3\text{C}_2\text{H}_5\text{Cl}$  and also  $\text{PCl}_3 + (\text{HO})_2\text{SO}_2 \rightarrow \text{P}(\text{OH})_2\text{Cl} + \text{SO}_2\text{Cl}_2$ .

This behavior, therefore, assists in the indication of the structure of compounds and is specially useful in organic chemistry. The products of these compounds present interesting variations, according to the element associated with the phosphorus and valency exhibited, but the student is referred for their detailed description to larger works (*vide* Roscoe & Schorlemmer, Abegg, etc.).

The sulfides of phosphorus also present a series of compounds made by direct union of phosphorus and sulfur in proper proportions. Of these, at least,  $\text{P}_4\text{S}_3$ ,  $\text{P}_2\text{S}_3$ ,  $\text{P}_4\text{S}_7$  and  $\text{P}_2\text{S}_5$  are distinct compounds. One of these has in recent years become of considerable importance as a substitute for yellow phosphorus in the manufacture of matches. It is known as the sesquisulfide,  $\text{P}_4\text{S}_3$ . It ignites at  $100^\circ\text{C}$ . and melts readily at  $172.5^\circ$ , and these properties make it suitable for use as a kindling material, while, as its high boiling point,  $408^\circ$ , indicates, it has a low vapor tension and lack of poisonous effect upon the factory workers.

## ARSENIC

**Occurrence.**—Arsenic occurs in many varieties of mineral forms. The most abundant is arsenical pyrites, mispickel,  $\text{FeAsS}$ . Other ores are: arsenite,  $\text{As}_2\text{O}_3$ ; orpiment,  $\text{As}_2\text{S}_3$ ; realgar,  $\text{As}_2\text{S}_2$ . Arsenides of several metals also occur, as  $\text{CoAs}_2$ ,  $\text{FeAs}_2$ ,  $\text{NiAs}$ , etc. Arsenic also is found as an impurity in most sulfide ores and hence in roasting and smelting operations its oxide is a constituent of the "fumes" and its disposal is a serious problem. The oxide is present in coal smoke and consequently in the atmosphere of cities, though, of course, only traces so occur. Since sulfide minerals are weathered by exposure, mineral waters and mine waters sometimes contain arsenical compounds. Arsenic also occurs in nature in native form.

**History.**—The compounds of the element were known to the early Greeks and the name arsenic is from *ἀρσενικόν*, meaning potent, probably by reference to the physiological effects. The element appears to have been isolated by the alchemist, Albertus

Magnus, about the middle of the thirteenth century. Brandt, the discoverer of phosphorus, showed the "white arsenic" of the pharmacist to be a "calx" of the metal and consequently when the nature of oxidation was cleared up by Lavoisier, it was recognized as the oxide. In the story of poisons arsenic finds a prominent place and the method of detection by Marsh, known as Marsh's test, was a valuable contribution to the limitation of its use in this manner.

**Preparation.**—In the roasting of arsenical ores, preparatory to smelting, the arsenic present is converted to the oxide and volatilized. It is collected in some cases in long, horizontal brick flues, while the gases pass on to the stack. A large portion of the arsenic of commerce is prepared from this source as a by-product of the smelting industries. The element itself may be obtained readily by reduction of the oxide with charcoal. It may be purified by sublimation. It is also prepared by heating mispickel in iron retorts and obtaining the arsenic as a sublimate,  $\text{FeAsS} \rightarrow \text{FeS} + \text{As}$ .

**Properties.**—Arsenic is a steel gray metal-like substance with a high luster. It tarnishes superficially in moist air to a dull, almost black surface. It has a specific gravity of 5.727. It is brittle. Like metals it is a good conductor of heat, though a poor conductor of electricity. It is readily volatile, *i.e.*, has a high vapor tension, at temperatures even much below its melting point, which under high pressure is about  $480^\circ$ . Its vapor density, 10.2 at  $860^\circ$ , corresponds to a molecular weight of 308.4, and since in arsenic chloride the amount of arsenic in a gram molecular volume is 75 g., the element is tetratomic, like phosphorus.

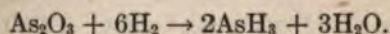
The arsenic vapor has the odor of garlic and is of a light yellow color. If cooled suddenly a yellow allotropic modification, analogous to yellow phosphorus, is obtained. It has a specific gravity of only 4.7. It is soluble in carbon disulfide, while the ordinary arsenic is not. When the ordinary arsenic is heated rapidly, a shining black crystalline modification is produced, which is considered to be another allotropic modification. The three varieties are sometimes distinguished as the  $\lambda$ -arsenic, the ordinary form;  $\alpha$ -arsenic, the yellow form, and  $\beta$ -arsenic, the black form. Arsenic burns readily with a bluish flame and garlic odor to form arsenic trioxide,  $\text{As}_2\text{O}_3$ . It unites readily with the halogens, with sulfur



and with many metals to form compounds. The latter may be considered either as alloys (*q.v.*) or as arsenides. It does not react with acids, *i.e.*, does not displace hydrogen ions, but with powerful oxidizing agents, such as aqua regia or nitric acid or even chlorine water it reacts to form arsenic acid,  $\text{H}_3\text{AsO}_4$ . This acid corresponds to the oxide  $\text{As}_2\text{O}_5$ . In this respect its behavior is analogous to that of phosphorus (*q.v.*).

**Uses.** — Arsenic is used in alloys as a hardening agent, particularly in shot, where it also serves the purpose of giving fluidity to the molten mass, so that the drops of molten alloy, as they are dropped from the shot towers into water, are more nearly spherical. It is, of course, used in making arsenic compounds, which are of extensive application.

**Compounds.** **Arsine.** — When metallic arsenides are treated with water or, more rapidly, with acids, arsine is formed, *e.g.*,  $\text{As}_2\text{Zn}_3 + 6\text{HCl} \rightarrow 2\text{AsH}_3 + 3\text{ZnCl}_2$ . It is also formed when arsenic compounds are treated with "nascent" hydrogen, *i.e.*, with an active metal and acid.



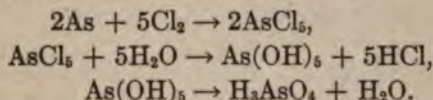
Since arsenic is a not infrequent impurity in both metals and sulfuric acid, the evil odor which sometimes accompanies hydrogen made by use of "commercial" materials is often due to the presence of traces of arsine. Arsine is a gas which may be condensed to a colorless liquid at  $-40^\circ \text{C}$ . It has a garlic odor and is intensely poisonous and at least one chemist paid his life as a forfeit in its investigation (Gehlen, 1815). If the gas is heated, it dissociates into arsenic and hydrogen and the reaction is but slightly reversible. This is the basis of the well-known Marsh's test, which is carried out as indicated in Fig. 80. In the generator zinc and acid free from arsenic are allowed to react until the apparatus is free from air. The arsenic solution is then added and the hard glass tube is heated with a burner. The arsine being dissociated, arsenic deposits just beyond the heated area (for full details consult texts on toxicology). Arsine reacts directly with silver nitrate to form metallic silver,  $6\text{AgNO}_3 + \text{AsH}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{Ag} + 6\text{HNO}_3 + \text{H}_3\text{AsO}_3$  (*cf. stibine*). Arsine differs from ammonia mark-



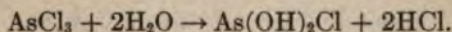
FIG. 80.

edly, not alone in its insolubility in water, but in that it does not unite with acids to form arsonium salts.

**Halides of Arsenic.**—Arsenic forms two series of derivatives in which it acts as a trivalent and pentavalent element, respectively. In the case of the halides only trivalent compounds are certainly known, except in the case of the pentafluoride,  $\text{AsF}_5$ . Arsenic trichloride may be made by direct action of chlorine upon arsenic and when an excess of chlorine is added, the pentachloride is perhaps formed, but if so, it decomposes at  $-28^\circ$ . It is most probable that the pentachloride does form at least evanescently, since by treatment of arsenic with chlorine water arsenic acid is formed and the simplest expression of the reaction is:



Arsenic trichloride is a colorless liquid with a boiling point of  $132^\circ$ , but which fumes strongly in the air, owing to its reaction with moisture. With cold water the reaction is



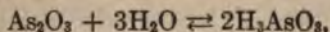
If the water and chloride are boiled together arsenious acid is produced, which, in turn, gives by dehydration arsenic trioxide. This behavior is, of course, in line with the general behavior of non-metallic halides.

**Oxides and Acids of Arsenic.**—When arsenic is burned in the air the normal product is the so-called trioxide which, while its vapor has a density corresponding to the formula  $\text{As}_4\text{O}_6$ , is usually formulated as  $\text{As}_2\text{O}_3$ . This is reasonable, since we have no accurate means of ascertaining the molecular weight of the solid oxide, and the solid form is the one ordinarily employed. It may be prepared in the vitreous or amorphous form by slow deposition of the vapor. By crystallization of the product of hydrolysis of arsenic trichloride, the crystalline trioxide is prepared. The amorphous variety changes on standing to the crystalline condition with evolution of heat and change of volume. There is also a second crystalline variety.

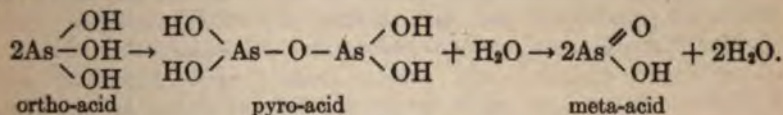
The vitreous oxide is very slightly soluble in water, about 3 parts per 100, and the solubility diminishes on standing, *i.e.*, the



crystalline material is less soluble. In solution we evidently have an equilibrium system as indicated:



though equilibrium is but slowly established at different temperatures. In general, the trioxide acts as an acid anhydride and hence if this system in equilibrium with solid oxide be treated with a base the solid dissolves by reason of the formation of salts of arsenious acid. The acid has not been isolated as such, but not only are its salts known, but the salts of the corresponding pyro- and meta-acids have been prepared. The relation between these acids is indicated by the formulæ:

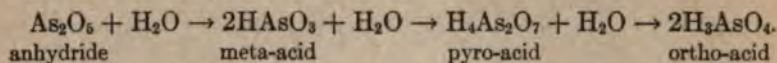


All arsenites except alkali arsenites are insoluble in water. All arsenites are reducing agents and in so acting are converted to arsenates (*vide infra*). Heated alone, arsenites give arsenates and free arsenic and are reduced by heating on charcoal to arsenic.

Arsenic trioxide is ordinarily known as white arsenic or more simply as "arsenic." It and the salts derived from it are used extensively in various ways. The trioxide is used as an insecticide, especially in the preservation of the skins of birds and animals in taxidermy, and in the manufacture of glass and enamels. The glasses containing arsenic oxide tend to crystallize to form white opaque glass, such as milk glass, etc. "Arsenic" is sometimes eaten by mountain climbers and others. It is said to steady the nerves and strengthen the respiration. It is also used in solution in sodium carbonate, *i.e.*, essentially sodium arsenite, as a medicine under the name "Fowler's Solution," as a remedy in nervous affections, such as chorea, etc. Scheele's green and Paris green, or Schweinfurt green will find mention later. (See copper compounds.)

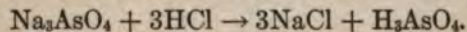
The pentoxide may not be prepared by burning arsenic in oxygen, as with phosphorus, but if arsenic acid be sufficiently heated it dehydrates, giving the pentoxide as a white, amorphous mass. If heated above a dull redness, it decomposes to the trioxide and oxygen. Like phosphorus pentoxide, the arsenic oxide dissolves readily in water, forming three distinct stages of

hydration. These are known as the ortho-, pyro- and meta-acids. The reactions may be formulated:

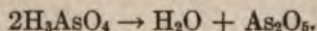


There is possible, of course, a fourth acid, the normal acid,  $\text{As}(\text{OH})_5$ , but, if formed at all, neither it nor its salts have been isolated. This series of acids offers no features other than those already discussed under phosphoric acid. Salts of the arsenic acids are used as insecticides in the form of tree sprays, the lead arsenates being most frequently used.

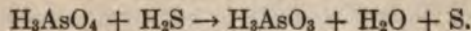
**Other Arsenic Compounds.** — Of the other arsenic compounds the most important are the sulfides, of which there are three. Realgar,  $\text{As}_2\text{S}_2$ , is a natural compound of orange red color. It is used as a pigment and also to make "white light" in pyrotechnics. It can be made artificially by subliming arsenical and iron pyrites. The trisulfide,  $\text{As}_2\text{S}_3$ , also is a natural compound and is formed by precipitation of arsenious compounds with hydrogen sulfide. If arsenious oxide solution is used, precipitation is slow, and a beautiful illustration of a colloidal solution is furnished. The powder is known as orpiment or king's yellow. When sulf-arsenates are treated with acid or when acid solutions of arsenates in hydrochloric acid are treated with hydrogen sulfide arsenic pentasulfide,  $\text{As}_2\text{S}_5$ , is precipitated. The precipitate also contains  $\text{As}_2\text{S}_3$ . The explanation of the precipitation of arsenic sulfides by  $\text{H}_2\text{S}$  is usually as follows: Arsenates are decomposed by mineral acids to form free arsenic acid.



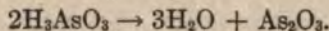
To some extent this suffers dehydration:



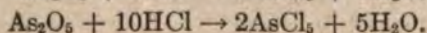
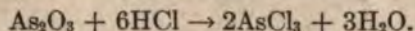
To some extent it is also reduced:



The arsenious acid readily dehydrates:

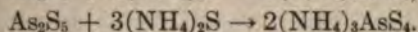
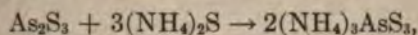


Both oxides react with acid to form salts:





The halogen salts furnish arsenious and arsenic ions, which then react with the hydrogen sulfide to form the corresponding sulfides. Both the arsenious sulfide and the arsenic sulfide are amphoteric in character and are more markedly acidic than basic. They dissolve only to a very slight extent in the strongest acids, but with basic sulfides react readily to form sulfur compounds analogous to the arsenious and arsenic acids. Thus:



The acids corresponding to these salts are unstable, giving the sulfides and hydrogen sulfide when acidified with strong acids. These reactions are extensively used in qualitative analysis as the basis of separation and identification of arsenic (*cf.* antimony reactions).

#### ANTIMONY

**Occurrence.**—Antimony in very small quantities occurs free, though associated with arsenic. Its most abundant ore is stibnite,  $\text{Sb}_2\text{S}_3$ , which is sometimes found in enormous spear-like crystals. Two naturally occurring oxides,  $\text{Sb}_2\text{O}_4$  and  $\text{Sb}_2\text{O}_3$ , are also known. A red ore of the composition  $\text{Sb}_2\text{S}_2\text{O}$  is known as antimony blende. Some antimony, like arsenic, is found in sulfur ores of other metals and is, therefore, found in the smelter fumes or flue dust as an oxide.

**History.**—Stibnite has long been employed by women of the orient as a cosmetic and medicine (2 Kings, 9:30; Ezekiel, 23:40). The methods of preparation and the properties, real and imaginary, were known to Basil Valentine, in the fourteenth century. Owing to the prominent place given to antimony in the *materia medica* of the middle ages, the element and its salts were well investigated by the iatrochemists, and Mellor remarks that by the end of the eighteenth century its properties had been more carefully investigated than those of any other element. He also quotes Valentine's awed remark: "He who would write of antimony needs a great consideration and a most ample mind. In a word, one man's life is too short to become acquainted with all its mysteries."

**Preparation.**—Antimony may be extracted from stibnite by heating with scrap iron,  $\text{Sb}_2\text{S}_3 + 3\text{Fe} \rightarrow 2\text{Sb} + 3\text{FeS}$ , the antimony being protected from oxidation by the molten slag of sulfide. It may also be "liquated," i.e., the crude ore is heated until the sulfide melts and runs off from the gangue. The liquated sulfide is then roasted for conversion to oxide, part of which sublimes. The oxide is reduced by charcoal. The crude antimony may be purified by melting with sufficient potassium nitrate to oxidize the impurities such as arsenic. A considerable amount of antimony is now prepared from the flue dust of the copper and lead smelters.

**Properties.**—It is a metal-like crystalline solid of high luster. It is very readily powdered and is frequently used in that form. It is a poor conductor of heat and electricity. It has a very high specific gravity, 6.7 to 6.8. It expands slightly on changing from the liquid to the solid state, a property which gives to it most of its uses as an element. It melts at  $629^\circ$  and boils at  $1440^\circ$ . It can be prepared in an allotropic form by slow oxidation of stibine at low temperature. (See also black antimony, Mellor, p. 606.) It tarnishes very slightly in moist air. It combines readily with the halogens, sulfur, phosphorus and arsenic. It is not acted upon by acids as such, but oxidizing acids convert it to insoluble oxides. Its atomic weight is 120.2. Its molecular complexity at the boiling point is three,  $\text{Sb}_3$ , though this may represent a mixture of molecules,  $\text{Sb}_4$  and  $\text{Sb}_2$ . The specific heat varies with the temperature, as is also true of carbon, boron, etc., being 0.046 at  $180^\circ$  and 0.0537 at  $300^\circ$ .

**Uses.**—Antimony is used to prepare the compounds of the element and particularly to form alloys such as type metals (Pb 25, Sn 5, Sb 20), Britannia metal (Cu, 3 Sn 40, Sb 7), shrapnel, etc. Powdered, it is also used to burnish plaster casts, etc. Antimony compounds were formerly very much used as a medicine, particularly as cathartics and emetics, and the metal itself as what were known as "everlasting pills." At the present time antimony compounds are not extensively used. For the composition of the alloys containing antimony, the reader is referred to the appendix.

**Stibine.**—Stibine is prepared precisely as is arsine (*q.v.*). There is this distinction between the properties of the two compounds.



Stibine is more readily decomposed by heat and the mirror of metallic antimony is closer to the flame used to form it. The spots formed by immersion of cold surfaces in the burning gases are blacker than those of arsenic and are not soluble in hypochlorite solutions and the reaction with silver nitrate produces not metallic silver, but silver antimonide,  $\text{SbAg}_3$ .

**Halogen Compounds.** — Of the halogen compounds only one, antimony trichloride,  $\text{SbCl}_3$ , need be mentioned. It was known to the iatrochemists and called "butter of antimony." It is a crystalline white solid, which deliquesces readily by absorption of water from the air, forming a pasty mass and finally a clear liquid. It is soluble in water and is hydrolyzed, giving antimonyl chloride, corresponding to the oxy salts of arsenic and bismuth. Antimony trichloride is used to some extent as a caustic in foot diseases of sheep, and to give the dull finish to gun barrels and other steel surfaces. The oxychloride,  $\text{SbOCl}$ , was formerly used as a medicine under the name of "powder of Algaroth." On boiling with water antimony trichloride hydrolyzes completely and the trioxide is formed. Antimony pentachloride is a liquid which fumes strongly in the air. In general, it behaves as does the pentachloride of phosphorus.

**Oxides and Acids of Antimony.** — Antimonious oxide,  $\text{Sb}_2\text{O}_3$ , is formed when antimony is burned, or by hydrolysis and subsequent dehydration of the chloride by water. It is more markedly a basic than an acid oxide, since it reacts readily with acids to form salts, of which the most important is a basic salt formed by boiling "cream of tartar,"  $\text{KHC}_4\text{H}_4\text{O}_6$ , with the oxide. From this solution crystallizes a compound having the composition  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ . It is known as tartar emetic and is the most important pharmaceutical preparation containing antimony which is at present in use.

If the antimony trichloride is hydrolyzed, the hydroxide,  $\text{Sb}(\text{OH})_3$ , is obtained, from which, by suitable treatment, meta-antimonious acid may be prepared. Both acids form readily hydrolyzed salts with bases. There are no special features of these relations not also presented by arsenious acid (*q.v.*).

Antimony pentoxide, like the corresponding arsenic oxide, is most readily prepared by heating the orthoantimonic acid. If heated above  $300^\circ$ , the tetroxide (*cf.* oxides of nitrogen) is formed. It dissolves in water very slightly, but the solution is acid. The pentoxide forms no salts with acids, *i.e.*, it is not basic.

Orthoantimonic acid is made by oxidation of antimony or its salts by strong oxidizing agents in solution. It separates out as a white powder, which is apparently partially the normal acid. The formula assigned is  $2\text{H}_3\text{SbO}_4 \cdot \text{H}_2\text{O}$ . On being heated to  $100^\circ$ , it is changed by loss of water to pyroantimonic acid, which has this distinction, that its sodium salt,  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ , is one of the few fairly insoluble salts of sodium. At  $175^\circ$  the pyro-acid loses another molecule of water, forming the meta-acid. A salt of this acid,  $\text{AgSbO}_3$ , is precipitated when silver nitrate is added to the strongly acid solution of antimony in nitric acid. This reaction is used in the identification of antimony.

**Thioantimonates.**—When antimony trisulfide is precipitated (this sulfide is orange-red when freshly precipitated, but when melted or as it occurs in nature is black), it is not readily soluble in ammonium sulfide  $(\text{NH}_4)_2\text{S}$ , *i.e.*, the trisulfide does not react as an acid anhydride to any considerable degree. It is soluble in the sulfides of the stronger alkalies (see Stieglitz, Qualitative Analysis). With addition of sulfur, or with yellow ammonium sulfide, soluble thioantimonates are readily formed, *e.g.*,  $(\text{NH}_4)_3\text{SbS}_4$ . These salts, on being acidified, liberate the free acid, which immediately decomposes, and the sulfide precipitates. The reaction is used in the separation of antimony, tin and arsenic sulfides from other insoluble sulfides. Sodium thioantimonate,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ , is a remarkably beautiful crystalline compound known as "Schlippe's salt."

### Bismuth

Bismuth occurs in very small quantities in the native state. Some occurs as the oxide,  $\text{Bi}_2\text{O}_3$  (bismuth ocher), and as the sulfide,  $\text{Bi}_2\text{S}_3$  (bismuthite or bismuth glance). Some bismuth is also found as a telluride. It is a comparatively rare metal and were it not for its use in alloys would doubtless be classed as such.

**Historical.**—Bismuth has been known for several centuries and was at first confused with antimony and with zinc. Its characteristics were first clearly defined in 1739. The name is of German origin, probably from "Weismuth," or "white stuff."

**Preparation.**—Bismuth is readily prepared by roasting the sulfide and fusing with charcoal. The crude bismuth is sometimes refined by melting on a slightly inclined iron plate, so that the



bismuth runs off into molds, "liquation," while the impurities remain on the plate or are volatilized. Occasionally impure bismuth oxides, formed as a sublimate in smelting ores of other metals, are treated with hydrochloric acid and the solution precipitated as the basic chloride by dilution with water.

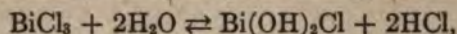
**Properties.** — Bismuth is a grayish white metal with a peculiar reddish tinge. It has a high luster. Its melting point is  $270^{\circ}$ . Boiling point,  $1435^{\circ}$ . Bismuth is stable in the air and tarnishes slightly, if at all, but on being strongly heated burns to the oxide,  $\text{Bi}_2\text{O}_3$ .

Bismuth is a very faintly amphoteric element. For the most part, despite its family relationships, it is characteristically metallic. At red heat it decomposes steam with liberation of hydrogen. It unites directly with the halogens. No hydrogen compound corresponding to arsine and stibine is known. It does not dissolve in acids as such, but is oxidized and converted to salts by the oxidizing acids. It alloys readily, especially with lead, which reaction gives rise to its most important applications. The metal itself is brittle and not ductile. The atomic weight of the element is 208.0, as deduced from the analysis of its chloride and from Dulong and Petit's law. The specific heat is 0.0303. The element is ordinarily trivalent, though in the form of oxides both tetravalent and pentavalent forms are known.

**Uses.** — The metal alone finds no practical applications, but by reason of its effect on the melting point its alloys find extensive use as type and fusible metals. The alloys of lead and bismuth alone or with cadmium and antimony also may be proportioned so as to melt at lower temperatures than any of the component metals alone. Thus Newton's metal (bismuth, 8 parts; lead, 5 parts; tin, 3 parts) melts at  $94.5^{\circ}$ . Wood's metal (Bi, 4; Pb, 2; Cd, 1; Sn, 1) melts at  $60.5^{\circ}$ . These and alloys of higher melting point may be used as safety plugs in automatic fire protection devices, electric connections, gas shutoffs, etc. The remarkable lowering of the temperature of fusion is but a specific case of the general effect of solutes on the lowering of the freezing point of solvents and emphasizes the character of alloys as solutions.

**Compounds.** — Only two of the many compounds demand special mention. These are the chloride and the nitrate. Bis-

muth trichloride,  $\text{BiCl}_3$ , is a white, crystalline, deliquescent solid. It is soluble in water, but hydrolyzes readily, and the reaction



is a strikingly interesting example of reversible reactions.

The hydroxychloride dehydrates even in water forming the oxychloride,  $\text{BiOCl}$ . It is used to some extent as a pigment under the name "pearl white," but its chief importance is as a factor in the identification of bismuth (see qualitative analysis).

Bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3$ , may be formed by solution of bismuth in strong nitric acid, but on dilution with water a basic salt is formed by hydrolysis, which is usually described as bismuth oxynitrate,  $\text{Bi}(\text{NO}_3)_3 + 2\text{H}_2\text{O} \rightarrow \text{Bi}(\text{OH})_2\text{NO}_3 + 2\text{HNO}_3$ . When dried it has the composition,  $\text{BiONO}_3$  and is very extensively used in intestinal troubles under the name bismuth subnitrate or "bismuth." A very interesting reaction is that sometimes used in surgery. Bismuth subnitrate is administered to a patient suspected of suffering from intestinal obstruction. The sulfur compounds in the intestinal tracts convert it to the insoluble bismuth sulfide, which lodges in the intestines and offers obstruction to the passage of X-rays through the body. An X-ray photograph may thus be taken, showing the location of the obstruction.

**Exercises.** — 1. With all the volatile compounds of phosphorus it is found that the weight of phosphorus present in a gram-molecular volume calculated at standard conditions is either 31 grams or an integral multiple of that amount. On the other hand, phosphorus vapor under like circumstances weighs 124 grams. What conclusions are to be drawn from these facts?

2. Prepare a drawing indicating the "cycle" of phosphorus in nature.

3. What volume changes occur when phosphorus is heated with (a) nitric oxide, (b) nitrous oxide, (c) nitrogen peroxide?

4. Formulate and compare the reactions between sodium hydroxide and phosphorus, sulfur and chlorine.

5. Given a specimen of calcium phosphate, how would you go about it to prepare (a) ammonium magnesium phosphate, (b) phosphine, (c) phosphorous acid.

6. What percentage of phosphorus pentachloride is dissociated when the gram molecular weight of its vapor is 156 grams.



7. On heating calcium sulfate with an excess of phosphoric acid to a red heat sulfuric acid is produced, what salt remains? Formulate the reaction.

8. Formulate the reactions between tertiary and secondary sodium phosphates and water to show why the solutions are alkaline.

9. The earliest matches were made of potassium chlorate, sugar and sulfur and were ignited by dipping in sulfuric acid. Formulate the reactions.

10. Compare the chemical and physical properties of the hydrides of nitrogen, phosphorus, arsenic and antimony.

11. Make a table showing the formulæ of the corresponding acids of nitrogen, phosphorus, arsenic, antimony and bismuth. Compare these acids with respect to stability and strength.

12. List the properties of the elements of this group and of their compounds which indicate (a) basic character, (b) acid character.

13. Formulate and explain the precipitation of  $\text{Sb}_2\text{S}_3$  from strongly acid solutions of antimonates by hydrogen sulfide.

14. How would you undertake to prepare Schlippe's salt?

15. Calculate the molecular weight of arsenic from the vapor density as given (p. 308). Why is this not a multiple of its atomic weight? How do we know what its atomic weight is?

## CHAPTER XVIII

### CARBON

THE carbon family contains but two members which are common elements and show predominating acidic character. These are carbon and silicon. The other members are either rare or characteristically basic. These two are extraordinarily interesting elements. Silicon is the element which is of second largest occurrence in nature and is the central factor in inorganic compounds. Carbon, on the other hand, is the fundamental factor in organic materials. Both elements are capable of taking part in an extraordinary variety of reactions and compounds, and anything like a complete discussion of the chemistry of either would carry the subject far beyond the limits of our present purpose.

Carbon and its derivatives are of such vast importance that their discussion forms a distinct subdivision of chemistry: Organic Chemistry. The detailed study of the natural forms of silicon compounds makes a very important chapter in Mineralogy. Nevertheless, neither element can be omitted from a discussion of general chemistry, not only because the discussion would be incomplete, but also because organic chemistry usually assumes a knowledge of certain phases of the chemistry of carbon, and Mineralogy seldom concerns itself with any of the vast number of derived forms of silicon compounds. It will, therefore, be the purpose of this and the following three chapters to present in brief outline some of these particulars.

**Occurrence.** — In the free form, carbon occurs in nature in three allotropic forms: diamond, graphite, and amorphous carbon. The diamond is a crystalline substance of the regular system and is rather sparingly distributed. The most important sources are South Africa, Brazil, India, Borneo, and Australia. Only one known source is in the United States — Arkansas. As found, the diamonds are usually in stream beds, whither they have been washed from the disintegrated "pipes" of heterogeneous rocky material, in which they were originally imbedded. In some localities they



are found in the original matrix. They are supposed to be of volcanic origin. The natural forms are usually water-worn or covered with a crust, which obscures their luster. The crystalline form bears no relation to the forms into which they are cut for use as jewels. (Fig. 81.) These shapes are varied, but are all designed to accentuate the reflection of light from interior surfaces. Various colors of diamonds are known. The "diamonds of the first water" are nearly or quite colorless, are practically pure carbon and are free from flaws. The colored varieties contain slight traces of foreign materials. When the diamonds are gray or black and more or less perfectly crystallized, they are known as "Boart" or "Carbo-nado." These imperfect forms



FIG. 81.

are used for abrasives or in cutting tools, though their importance has diminished in this direction through the synthesis of carborundum (*q.v.*). The Cullinan is the largest known diamond, weighing over a pound and a quarter. The most noted diamonds previous to the discovery of the Cullinan (1905) were the Jubilee, weight 49 grams, and the Kohinoor, 22 grams.

The diamond is sold by the "carat," a term derived from the carat bean formerly used as a unit of weight by the diamond dealers of India. A carat equals 0.207 grams.

Graphite is of wide distribution and is sometimes found in large deposits, notably in Ceylon, Canada, etc. It also occurs in many meteorites, in a few of which diamonds are also found. Its crystals are soft, leaf-like plates of the hexagonal system. The substance is also known as "plumbago" and as "black lead," these names being due to the erroneous impression that it contained lead.

Amorphous carbon is the term applied to all varieties of the element in which crystalline structure is not apparent. It includes charcoal, coke, soot, etc. Natural deposits of pure or approximately pure amorphous carbon are not known, but since it is produced by the imperfect combustion of fuels, such as coal, petroleum, etc., it is present in small quantities in the atmosphere of cities. Impure amorphous carbon is extremely abundant in

nature, the purest form being the better grades of anthracite coal, which sometimes run as high as 95% carbon. The various grades of coal are produced by the more or less complete transformation of vegetable material. This metamorphosis has taken place through the effect of pressure and heat and slow oxidation of deposits of vegetable material and, in addition, these deposits contain greater or smaller quantities of mineral matter deposited at the same time. (For full details of the origin of coal deposits see geological references.) Coal, therefore, according to source and degree of transformation, contains varying quantities of carbon, hydrogen, oxygen, nitrogen, and of the other constituents of wood and of mineral matter. Indeed, deposits of all degrees of metamorphosis and of purity are known. These varieties are classified and their typical composition is shown in the table below, and for comparison the composition of wood is also given. Coke and charcoal are usually artificial, but natural deposits are known.

	Percentage, excluding ash and moisture.				Ash.	Water.
	C.	H.	O.	N.		
Wood.....	45	6	48	1	1.5	18-20
Peat.....	60	6	32	2	5-20	20-30
Lignite.....	70-75	4.5-5.5	16-24	1-2	3-30	15
Bituminous.....	83.5	5.3	9.5	1.7	10-12	8
Semi-bituminous.....	91.5	4.4	3.0	1	6.5	3-4
Anthracite.....	94	3	3	0.5	2-10	2
Charcoal.....	84-90	1.25	3-15	....	2	0-6
Coke.....	95	0.5	3	1	4-15	0-2

Carbon also occurs in nature in a bewildering variety of compounds, both of inorganic and organic type. Attention has been already called to the essential presence of hydrogen, oxygen, nitrogen, and sulfur in all bodies of matter possessing auto-locomotive power. The fifth essential, the quintessence as it were, is carbon. Indeed, all organic compounds contain carbon and hydrogen at least. (By the term *organic* compound, we refer to all substances composing or produced by living organisms. It is true that through synthesis we are able to produce many of these substances artificially and also true that many synthetic compounds of carbon have been produced which are unknown in



natural organisms, yet in all if termed organic, the element carbon appears. Hence their study is included in organic chemistry.)

Included, then, among organic compounds occurring in nature we have not only living plants and animals, but many carbon-bearing compounds produced by their decomposition. The most important of these are the great groups of substances included under the terms petroleum and natural gas. Of these more anon. Mention has also been already made of carbon dioxide (*vide* atmosphere) as a constituent of the atmosphere, vast quantities of which by virtue of its solubility are present in the waters of the earth. Carbonates are so abundant that certain mountain ranges are almost wholly composed of them and numerous more or less isolated deposits occur. The more important carbonates are dolomite,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ ; limestone,  $\text{CaCO}_3$ ; magnesite,  $\text{MgCO}_3$  and siderite,  $\text{FeCO}_3$ . Besides these there are numerous other carbonate ores. With mention even thus relatively briefly of the natural forms of carbon, it is rather surprising that carbon comprises only about 0.19% of the total components of the earth's crust and that eleven other elements are more abundant.

**Preparation.** — Amorphous carbon is prepared in three special forms: charcoal, lampblack, and coke. The same principle is employed in all cases, volatilization of the constituents, other than carbon, by heat so far as such is possible. In all cases mineral constituents remain with the carbon. The raw material for charcoal is usually vegetable material, mainly wood. The distillation is carried out in two ways. The older method is to cover the wood in the form of heaped logs or billets with sod or earth, leaving a few openings for air. The wood is fired and allowed to burn slowly, so that the combustion of a part furnishes the heat to drive off the volatile constituents of the remainder. All the volatile constituents are either burned or lost in this method, and 80% to 90% of the wood is destroyed. The volatile material, consisting chiefly of gases, water, and smaller amounts of alcohol, acetic acid, etc., are saved by the more modern method of distillation in retorts. The residue varies in composition and quality according to method and temperature employed. The finest charcoal is made from willow wood. Several commercial varieties are distinguished because adapted for special purposes, such as the exceptionally pure carbon made by heating pure sugar — sugar charcoal. Considerable quantities of animal charcoal are

made by heating bones, blood, etc., in closed retorts (see uses of charcoal). The variety known as ivory black is animal charcoal from which the mineral matter has been removed by means of hydrochloric acid. Coke is prepared from coal, the bituminous variety, by distillation of the volatile factors, both in the "bee-hive" oven and in closed retorts (see *Sci. Am.*, Vol. 112, p. 379). In the former, the volatile constituents, coal tar, gases, etc., are lost. In the latter, they are frequently the materials sought (Fig. 82). The manufacture of coke and its by-products is one

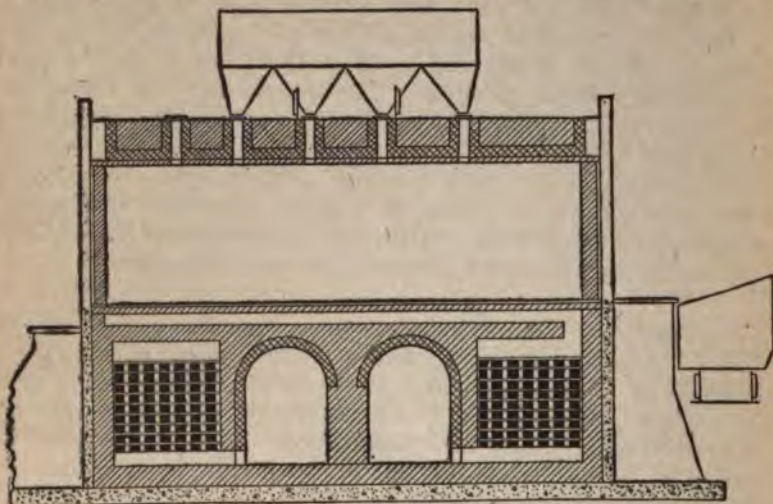


FIG. 82.

of the great industries, both by reason of the extensive applications of coke (*q.v.*) and because of the value of the gas and tar (*q.v.*). Lampblack is made by the imperfect combustion of petroleum or natural gas, and various systems for the practical performance of the task are employed.

Graphite is now manufactured on a commercial scale by what is known as the Acheson process (1907). Coke, or charcoal, and coal tar are ground together to form a pasty mass, which is molded into the desired form and then heated, out of contact with the air, to the highest temperature possible, by means of an electric furnace. On account of the extensive and growing practical uses of graphite (*q.v.*), this industry is of increasing importance. Vast quantities of graphite are manufactured in-



eident to the preparation of pig iron, which contains about 4% of it.

Diamonds were first prepared artificially by Moissan (1887) by dissolving carbon in molten iron and suddenly cooling the solution by plunging the molten mass into cold water. The outside of the mass being thus hardened, the inner portion solidified more slowly and under immense pressure since solidification of the mass is with increase of volume. The diamonds so produced were of almost microscopic dimensions, and the method has not been developed to practical operation. It is chiefly interesting as showing how diamonds are undoubtedly formed in nature.

**Properties, Physical and Chemical.** — The specific gravity of the diamond is 3.5 with a small range of variation among the different kinds. It is the hardest of known substances and is insoluble to any marked degree in any solvent at ordinary temperatures. It is also unaffected by acids or most oxidizing agents. When pure, it is transparent and has a very high refractive index, 2.417 for sodium light, and very great dispersive power. As used, the natural octahedral or the water-worn material, is cut in order to accentuate these light effects and give to it the power to reflect and refract light, and furnish the sparkle and brilliant colors which, together with its rarity, make it prized as a jewel. The diamond, unlike glass, which is frequently used as an imitation under the name of *paste* or *strass*, is transparent to X-rays and fluoresces in the dark when brought into the neighborhood of radium or other radioactive substances. These properties, together with its hardness, render detection of such imitations rather simple. When treated with very powerful oxidizing agents at high temperatures, the diamond is slowly oxidized. When heated in the air to from 800° to 900° it burns with difficulty and if the diamond be pure, the product is carbon dioxide. Of course, impure samples yield varying quantities of ash. If heated in the absence of air, it remains unchanged until a temperature approaching 2000° is reached, when it swells and becomes a black graphitic mass.

Graphite has a specific gravity of about 2.3, though the various natural forms show specific gravities ranging from but little more than that of amorphous carbon to nearly that of diamond. As already mentioned, it is made up of more or less definitely formed monoclinic crystals in six-sided leaflets. The leaflets are very smooth and soft and move over each other with little friction.

The material also clings readily to surfaces of wood or iron and is unchanged by heating. These properties are utilized in lubrication of wooden or iron bearings, in the latter case especially when high temperatures are involved. At high temperatures it is the most stable form of carbon. It will burn a little more readily than the diamond, ignition temperature about  $700^{\circ}$ , but is still very difficult to burn, especially when mixed with clay. It is oxidized by reagents more readily than the diamond and when treated repeatedly with a pasty mixture of potassium chlorate and nitric acid at  $100^{\circ}$  is converted to a yellow mass known as graphitic acid, of uncertain composition. This treatment leaves the diamond unaffected and converts amorphous carbon to a soluble brownish material. Natural graphites give, on burning, carbon dioxide and usually a very considerable percentage of ash.

Amorphous carbon is practically never pure, even sugar charcoal retaining a trace of hydrogen. Its specific gravity varies from 1.45 up to nearly the specific gravity of graphite, according to the material and method used for its preparation. It usually varies between the limits of 1.70 to 1.90. It is probable that no sample is a pure chemical individual. Since it, as the diamond and graphite also, is insoluble in all solvents suitable for the purpose, we know next to nothing of the molecular complexity of the different forms. Also as a necessary consequence of the modes of preparation it has widely varying proportions of foreign material, ranging from nearly 90 per cent in bone black to traces in sugar charcoal. By consequence of these variations, it is difficult to assert definite properties without undue circumlocution. In general, however, it is characterized by a large absorptive power for gases and also for many varieties of coloring and other soluble materials. This is particularly true of animal charcoal, from which the calcium and other phosphates have been removed by treatment with acid. The amounts of the gases so absorbed are greater the lower the temperature, and are also greater with the more easily liquefiable gases. Thus, a given variety of charcoal has been shown to absorb 171 volumes of ammonia, 65 of carbon dioxide, or 15 of nitrogen, at  $0^{\circ}$ , while at  $-185^{\circ}$ , it will absorb 230 volumes of ammonia. By contrast with platinum and palladium, it absorbs very small volumes of hydrogen. The absorbed gases are, probably by reason of increased concentration, more active chemically than in the free condition. This absorptive power leads to many interesting uses (*vide uses*).



Carbon has, according to the type used, an ignition temperature varying from 300° up to nearly that of graphite. Indeed, due to occlusion of oxygen from the air, sufficiently finely divided charcoal may ignite spontaneously, *i.e.*, the slow reaction at first initiated may produce sufficient heat to induce rapid combustion. This is a very serious factor in the storage of large masses of fine coal. The product of its reaction with oxygen is, according to the temperature employed or the relative proportions, either carbon monoxide or the dioxide. (*Vide* carbon dioxide.) Since the affinity of carbon for oxygen is great and the product is a gas (*vide* equilibrium), it will, at high temperatures, remove oxygen from many metallic oxides. For this purpose either charcoal or coke or some other form of carbon may be used, but the porosity, hardness and convenient sizes of coke renders its use in the huge iron furnaces especially practicable. At high temperatures, carbon unites with many elements and when these are metals the products are called carbides (*q.v.*). It also unites with hydrogen (*vide* acetylene), nitrogen (*vide* cyanogen), sulfur (*vide* carbon disulfide), silicon (*vide* carborundum), etc.

**Uses.**—Clear and flawless diamonds are used for jewels. Inferior diamonds are used for cutting glass and for diamond drills and for such work as requires a very hard abrasive material. In this connection, carborundum and artificial boron are being substituted. Graphite is, as already mentioned, used extensively as a lubricant in bearings likely to heat and in chain bearings, such as those on bicycles. It is mixed with fine clay or other cementing materials to make lead pencils,\* hence the name (from  $\gamma\rho\alpha\phi\omega$  = I write). Also mixed clay, sand and graphite in the ratio of 75 : 25 : 100 is used to make crucibles for the manufacture of crucible steel and other metallurgical processes where a high degree of refractoriness is needed. In the form of large sticks it is used to make the electrodes for electric arc lights, electrolytic processes, etc. This use is extended to the manufacture of electric furnaces, both of the arc and of the resistance type. In the latter case, the graphite is mixed with carborundum and clay, or with infusorial earth or with alundum (*q.v.*) Because of the moderate conductivity of the graphite as indicated by its applications just mentioned, it is also used to coat non-conducting

\* The world's production of lead pencils is 2,000,000,000 yearly and of the United States 750,000,000.

surfaces which are to be electroplated. It is also used for stove polish, polish for gunpowder, etc.

Amorphous carbon finds such an enormous variety and extent of practical application as almost to prevent an attempt at enumeration. Most of these applications depend upon the equilibrium between carbon and its compounds and oxygen. Because of this the system needs only to be heated in order to produce formation of carbon monoxide or carbon dioxide, and since the reaction is exothermic (see heat of combustion), carbon in the various forms from wood to coke finds its chief application in the production of heat, both for domestic and power purposes. For the same reasons, enormous quantities of coke, charcoal and coal are used in metallurgical processes to reduce the oxides of metals. Coal is also used to produce gas by distillation (see coal gas). Lampblack is used in enormous quantities whenever a black pigment is desired, such as in printer's ink, shoe and stove polish, paints, etc. Animal charcoal is used to remove coloring matter and dissolved gases from liquids and hence finds application in the refining of sugar and similar operations. Charcoal filters for water are frequently employed. This absorptive power of carbon for gases at low temperatures is employed in a very interesting case, the production of very high vacua. Sewers and other foul places are purified by addition of charcoal by utilization of this same property, and charcoal is used medicinally for the same reason. It will be seen, therefore, even from the above hasty résumé, that carbon in its varied forms and degrees of purity holds an unrivaled place among the elements in its adaptability to human needs and desires.

***The Dioxide and Carbonic Acid.*** — Carbon forms two well-known oxides, carbon dioxide and carbon monoxide. There is certainly one other oxide, carbon suboxide,  $C_3O_2$ , and at least two others are reported, but attention is not directed to these last because of relative unimportance. The dioxide and monoxide, however, play very important rôles and will be somewhat fully discussed. The dioxide occurs in vast quantities in the air. While the percentage content of the sea and surface waters is small, in the aggregate, vast amounts are present in water. Many springs which have access to subterranean sources of the gas are highly charged with it, and when the water reaches the surface, the escape of the gas causes the phenomenon of effervescence.



There are many sources of carbon dioxide in the form of gas springs and volcanoes. In certain localities it is constantly supplied at a rate greater than its rate of diffusion and, since it is heavier than air, it flows downward like a stream. This is the case in the famous Grotto del Cane near Naples. This accounts for its accumulation also in old wells, mines, etc. Its compounds, the carbonates, are of enormous extent in nature, the most common forms being the carbonates of calcium (limestone, calcite, aragonite, etc.), magnesium carbonate, and the double salt, dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). The carbonates of many other metals are also more or less common minerals.

It is certain that carbon dioxide was recognized long ago, but its definite recognition as a chemical individual we owe to Dr. Black, a Scotch scientist, in 1755, who called it "fixed air" because absorbed by the caustic alkalies. Lavoisier recognized its chemical nature as an "acid," or as we say, an anhydride, and showed it to be an oxide of carbon.

It is formed when carbon or carbon compounds are burned with free access of air at not too high a temperature. It is also formed when limestone is heated to manufacture lime, and it is occasionally collected from this source. It is formed in the process of fermentation of sugar by yeast in the manufacture of bread, beer, wine, etc., the other product being alcohol. Frequently, the carbon dioxide is collected for use from the product of the beer vat. It is, of course, a product of the combustion of animal tissue and is present to an extent of about 4 per cent in expired air. In the laboratory, it is prepared usually by treatment of a carbonate with an acid. Most common acids, even acetic, are strong enough to displace carbon dioxide at a reasonable rate unless the salt formed protects the carbonate from the action of the acid, as is the case with limestone and sulfuric acid. Mineral carbonates are less readily decomposed than are freshly formed samples of like type.

The gas is colorless and odorless, though when inhaled through the nose it gives a tingling sensation, due probably to its solution as carbonic acid. It has a pleasant acid taste. Its specific gravity is 1.529 and consequently it diffuses very slowly and may, therefore, be collected by displacement of air without very great loss. Its critical temperature is  $31.1^\circ$  and the critical pressure is 77 atmospheres. (See Fig. 83.) It will be noted that the pressure required to keep it liquid at ordinary temperatures is very considerable and hence the liquid is kept in very heavy iron cylinders. The

boiling point of the liquid is  $-78.2^{\circ}$ . The latent heat of vaporization of the liquid is, at  $0^{\circ}$ , 57.5 cal. per gram. When the liquid evaporates, if heat is not supplied rapidly, the temperature is lowered in the residue to the freezing point, which is at atmospheric pressure only  $-79^{\circ}$ . The solid carbon dioxide is a snowlike mass, which sublimates readily, and by reason of the heat absorption of

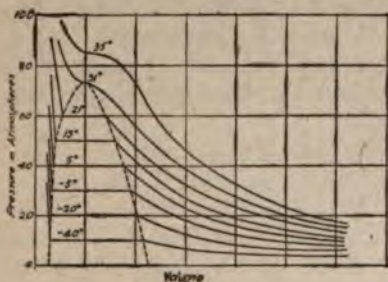


FIG. 83.

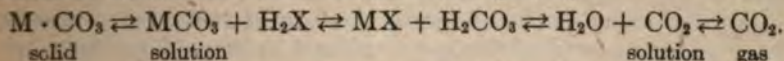
the process it proceeds but slowly in the air. The snow may, therefore, be handled in various ways, which seem very remarkable, considering the very low temperature of the substance. The solid contracts on melting and hence the melting point is raised by pressure, being only  $-56^{\circ}$  at a pressure of 5 atmospheres. The solid is a poor conductor of heat. It dis-

solves readily in ether, chloroform or alcohol and these solutions are extraordinarily good freezing mixtures and with them temperatures approaching  $-110^{\circ}$  can be obtained. By use of reduced pressure, to induce rapid evaporation, the temperature may be lowered even to  $-140^{\circ}$ .

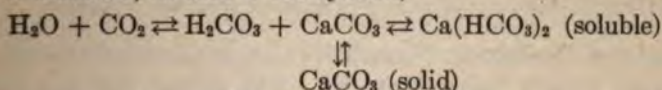
Carbon dioxide has at  $15^{\circ}$  a solubility in water of 1 cc. per cc. of water and increases nearly in accord with Henry's law until four to five atmospheres is reached. At higher pressures the rate of solution increases. When saturated solutions have opportunity to liberate gas, the rapid escape of gas bubbles carries minute droplets of water a short distance above the liquid surface, the return of which gives rise to the rainlike appearance known as effervescence. The saturated solution at from 2 to 3 atmospheres is known as "soda water" because the carbon dioxide used was originally prepared by use of sodium bicarbonate and sulfuric acid. The same phenomenon, effervescence (and accompanied by the formation of bubbles, froth, when any increase of viscosity is produced by use of other solutes), occurs in carbonated liquors such as beer, champagne, etc., in which the carbon dioxide is present for the sake of its own pleasant taste, as well as to mask the insipidity of the liquors. The solution in water is a fairly acid substance and presents the equilibrium system  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{H}'\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{CO}_3''$ . The same remarks apply,



with suitable modifications, to this system as were made concerning the ammonia and sulfur dioxide systems (*q.v.*) It reacts as a dibasic acid and the neutral salts are readily hydrolyzed in solution because of the weakness of the acid (*vide* p. 183). The carbonates of all the metals other than those of the alkalis are but slightly soluble in water, but consideration of the system,



would indicate that they are readily soluble in acids. The acid salts or bicarbonates are more soluble than the neutral salts and are also unstable, so that if the system,

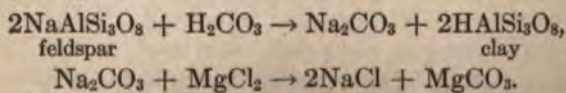


is subjected to increased pressure of carbon dioxide, increased quantities of the acid carbonate are formed. When the carbon dioxide pressure is diminished, the system moves to the left. These considerations explain the formation of "hard" water in limestone or other mineral carbonate regions and the discharge of this type of hardness by boiling. They also account not only for the formation of caves such as the famous Mammoth Cave of Kentucky and the "Sinks" of Florida, but also for the stalactites and stalagmites which so weirdly decorate such caves (*vide* also water softening).

Carbon dioxide itself is a very stable substance, beginning appreciably to decompose only at relatively high temperatures, *e.g.*, at 1300°, the decomposition is only 0.004 per cent and at 1500° about 0.5 per cent. This system,  $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$  is, however, made to move in the direction  $\rightarrow$  when oxygen-consuming materials are present (*vide* carbon monoxide). This is, of course, only materially possible at high temperatures. Since carbon dioxide represents the maximum oxidation of carbon it cannot burn and because of its stability it is not a supporter of combustion, hence it cannot support respiration and, by exclusion of the essential oxygen, if inhaled, produces, or tends to produce, suffocation. The discussion of the varied properties of carbon dioxide foreshadows the practical applications. Being a by-product of so many reactions and of such varied and extensive occurrence in nature, its cost is solely dependent upon the difficulties attending its collection and control. At present it is used commercially for the most part as a liquid. The cylinders of liquid are prepared at suit-

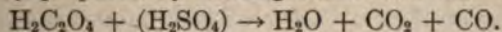
able locations, great breweries, lime kilns, natural springs, etc., and thence shipped for use in the preparation of soda water and other effervescent drinks, some of which are artificial mineral waters made in imitation of natural carbonated waters. Carbon dioxide is also manufactured, as used, in "chemical engines" and hand fire extinguishers. The materials employed are usually sodium bicarbonate and sulfuric acid or alum and the pressure produced by the development of the gas is utilized to force the stream upon the burning bodies. It functions in this connection chiefly by displacement of the oxygen. The liquid dioxide is used as a refrigerant on shipboard, where the use of ammonia for this purpose is undesirable because of odors produced through leakage.

**Cycle of Carbon in Nature.** — Carbon dioxide is decomposed by plants, oxygen being liberated. The energy required for this reaction is derived from sunlight and the suitable conditions are supplied by chlorophyll. Apparently the first step is  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{O}_2$  and the first product, formaldehyde, is, by polymerization and by partial dehydration of the polymerized products converted into cellulose, starch, sugars, etc. These materials are then utilized by animals. This withdrawal of carbon dioxide from the air would ultimately cause plant starvation except for the replacement due to decay, respiration, combustion, etc., and the supply from subterranean sources. A portion of the total withdrawal is permanent, except in geological sense, in two ways: First, a greater or smaller amount of organic material is enabled to escape decay through deposition under water and the formation of the series of metamorphoses — wood  $\rightarrow$  peat  $\rightarrow$  soft coal  $\rightarrow$  hard coal. These supplies are Nature's "conservation for posterity." Second, soils are formed by the decay of rocks and the disintegrating factors, oxygen and carbonic acid, acting under varying temperature and consequent volume and rate changes, produce the insoluble soil constituents, and carbonates which are soluble. These soluble carbonates ultimately find their way to the sea, and there produce insoluble carbonates. These are now unavailable for Nature's uses until the next geological epoch. The reactions involved are fairly complex, but may be typified by the following:

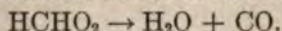




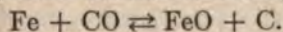
**Carbon Monoxide.**—This substance seldom occurs in nature,\* but is formed when carbon is burned in an air supply insufficient to produce the dioxide. It is formed in great quantities in a number of industrial operations, of which the most important are the smelting of iron and the manufacture of water gas and producer gas (*q.v.*). It is to be observed burning with a blue flame over the heated surface of a coal fire. In the laboratory it is ordinarily prepared by heating oxalic acid with sulfuric acid:



The sulfuric acid is used as a dehydrating agent. The dioxide is absorbed by passing the gases through alkaline solutions. Formic acid may be employed instead of oxalic acid, in which case only carbon monoxide is obtained and heating is unnecessary,



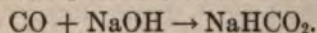
The gas is colorless, tasteless, odorless, and practically insoluble in water (3 vol. to 100). Its specific gravity is 0.9672, or practically that of air. Its molecular weight is, therefore, 28. It liquefies under atmospheric pressure at  $-190^\circ$  and is solid at  $-203^\circ$ . It is intensely poisonous and very minute concentrations of it in the air will cause illness and death if inhalation is protracted. The time required for the production of serious symptoms naturally is shortened by increased concentrations. Many fatal accidents are due to it, since imperfect combustion may readily take place in stoves, gas heaters, charcoal braziers, etc., and because it is a constituent of fuel gases (*q.v.*). It is also used with suicidal intent. The poisonous behavior of the gas is apparently due to its property of combining with the hæmoglobin of the blood to form a slightly more stable compound than oxy-hæmoglobin and which is not decomposed by the tissues which are oxidized by the latter. The sufferer is thus effectually suffocated, even in the presence of abundant oxygen. The gas burns readily in the air, producing carbon dioxide. This action is reversible at high temperatures, and in consequence the oxide is formed when carbon dioxide is heated in the presence of carbon, iron, zinc, etc. In general, the oxide is stable and will not give up its oxygen readily, but if heated with iron, the oxide is reduced:



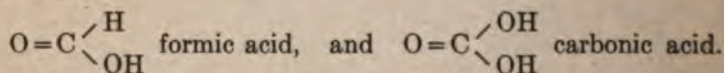
\* Langdon (Jour. Am. Chem. Soc., Vol. XXXIX, p. 149, 1917) has shown that the gas contained in the floaters of the giant kelp contains quantities of carbon monoxide varying from 1 to 12 per cent.

This action begins as low as  $330^{\circ}$ , and is facilitated by increase of temperature, but less rapidly than the reverse action. This behavior of the monoxide is of importance in the smelting of iron (*q.v.*).

Carbon monoxide, since its molecular weight is 28, has the composition CO and the structure appears to be  $C=O$ . The carbon is, therefore, bivalent. Carbon in the vast majority of its compounds appears to manifest a valency of four. It is not surprising, therefore, that the monoxide may unite directly with certain elements and with other unsaturated compounds. These compounds are known as carbonyls (*cf.* antimonyl, bismuthyl, etc.). Thus, it unites with the vapor of sulfur to form carbonyl-sulfide,  $S=C=O$ ; with chlorine to form carbonyl chloride, otherwise known as phosgene,  $COCl_2$ ; with nickel to form  $Ni(CO)_4$ ; with iron to form  $Fe(CO)_4$ , etc. (*cf.* nitrogen monoxide and peroxide). These carbonyl compounds are of great interest and considerable theoretical and practical importance, but the student is referred to fuller texts for details. Carbon monoxide may be regarded as the anhydride of formic acid, but the reaction between it and water is very slight indeed. If it is passed over palladium black when cold and moist, traces of formic acid are formed. The formates are fairly readily made by heating it with sodium hydroxide, under pressure, to from  $200^{\circ}$  to  $230^{\circ}$ :



We must, however, recognize a distinct difference between "carbonous" and carbonic acid. Their structures are perhaps best indicated by



The use of carbon monoxide is largely as a constituent of gaseous fuels and the varieties will be briefly discussed in another place. (See p. 348.) When carbon is burned, the heat evolved is 94,310, 94,810, or 97,650 calories, according as diamond, graphite or charcoal is consumed to form carbon dioxide. When carbon monoxide is formed from charcoal the heat evolved is 29,650 calories, and the second step, the burning of carbon monoxide to dioxide, therefore produces 68,000 calories. In spite of the fact that about 30 per cent of the fuel value of carbon is lost when converted into carbon monoxide, it finds use as a fuel, since, by reason of

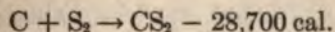


superior convenience in handling, better adjustment of heat source to surface heated and better control of heat produced, such transformation is of economic advantage. (See gaseous fuels.)

**Carbides.** — When carbon is heated with oxides not only may reduction take place, but, if the temperature is satisfactory, union between the carbon and the reduced substance may take place. This result has long been reached in the smelting of iron (*q.v.*). The "combined carbon" which exists in varying proportions in cast iron and steel is probably of the composition  $\text{Fe}_3\text{C}$  and is called cementite. In recent years the production of carbides by means of the electric furnace has assumed great importance because of the valuable properties of these substances. Calcium carbide,  $\text{CaC}_2$ , is made by heating calcium oxide with carbon in an electric furnace, to an estimated temperature of about  $3000^\circ$ . The carbide produced is a hard, brittle substance with a specific gravity of 2.2. It finds application by reason of the fact that when heated in nitrogen, it forms calcium cyanamide (*q.v.*), and that when placed in water it forms acetylene (*q.v.*). Silicon carbide,  $\text{SiC}$ , known as carborundum, is also formed in the electric furnace by heating coke and sand to the estimated temperature of  $3500^\circ$ . It is a substance of very remarkable properties. It is unattacked by acids. It is practically infusible, and is nearly as hard as diamond. It finds extensive application as an abrasive.

**Other Compounds of Carbon.** — The compounds of carbon and hydrogen with their derivatives are so numerous and important that even a brief résumé demands a separate chapter. The compounds with the strictly non-metallic elements are not called carbides. Of them only three will require special mention. These are carbon disulfide and carbon tetrachloride and cyanogen.

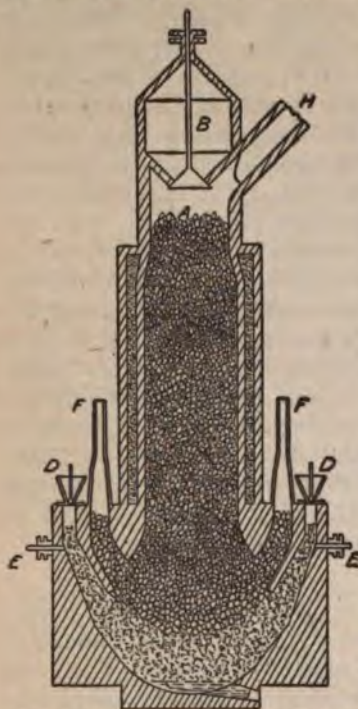
The disulfide is manufactured almost wholly by Taylor's electric process (1899). (Fig. 84.) The reaction is endothermal:



The formation is, therefore, favored by rise of temperature, and by sudden cooling the reverse action is inhibited. The furnace is heated by an alternating current and the volatilized sulfur passes over hot carbon. The product is contaminated with free sulfur, and may for many purposes be used in this form. It may be

purified by redistillation and sundry other methods. When pure, it is a colorless, mobile, highly refractive liquid (index 1.643 at 0°). It has an aromatic odor, but the commercial variety has a very offensive odor. It is very poisonous. If inhaled in the form of vapor it produces serious symptoms. It is quite insoluble in

water (0.258 gram per 100 cc. at 0° and 0.101 gram at 20°). Its specific gravity is 1.292. Its boiling point is 46°. Its vapor is very easily ignited, the kindling point in air being about 40°. Its mixtures with air are very explosive by reason of the heat liberated, and these properties, coupled with its slow diffusion, render its distillation, or use, in the neighborhood of flames dangerous. It is an extraordinarily excellent solvent for many substances such as iodine, phosphorus, sulfur, camphor, gums, resins, fats, waxes, rubber, etc. It is also miscible in all proportions with alcohol, ether, benzol, and the essential oils. Its properties render it an extremely useful substance, and it is especially largely employed as a solvent. A very interesting consequence of its cheap production in commercial form by Taylor's process is its use as a vermifuge, particularly in reclaiming large areas of land formerly occupied in the Great Plains by prairie dogs. An interesting minor use is

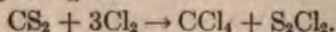


*DD Sulphur Hoppers H Outlet to Condenser  
EE Current Inlets B Charcoal Hopper  
FF Carbon Rods A Charcoal Bed*

FIG. 84.

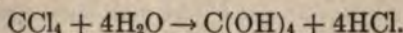
in glass prisms as a dispersion agent for light. The salts of thio-carbonic acid are known and it is therefore, properly regarded as a thioanhydride.

Carbon tetrachloride is most readily made by treatment of carbon disulfide with chlorine, using antimony trichloride as a "carrier" or catalytic agent.

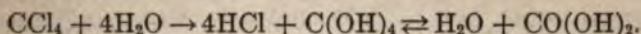




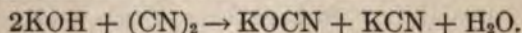
The other carbon halides may be made in a similar manner, as well as by various other processes. The interest attached to the tetrachloride is its utility as a solvent of fats, etc., and because of its non-inflammability and its boiling point,  $76.7^{\circ}$ , being notably higher than other suitable substances, its use as a dry cleaning agent is rapidly increasing. The trade name is carbona. Its hydrolysis in water should produce normal carbonic acid:



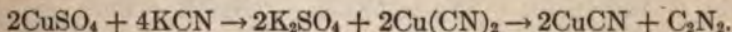
This substance is not known, but a derivative, ethyl orthocarbonate,  $\text{C}(\text{OC}_2\text{H}_5)_4$ , is. It, therefore, is reasonable to suppose these relations obtain:



Cyanogen  $(\text{CN})_2$  is formed by direct union at high temperatures and it consequently is a constituent of blast furnace gases and is also formed in coke and coal gas manufacture. It may be prepared by the discharge of electricity between carbon poles in an atmosphere of nitrogen. Because it is a highly endothermic compound, the decomposition is usually nearly complete unless sudden cooling slows the reverse action. It is a highly poisonous gas, capable of very varied reaction. It behaves in some respects as does chlorine. Thus, with potassium hydroxide it gives:

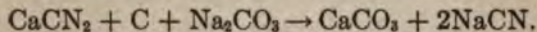


For this and similar reasons it is sometimes symbolized  $(\text{Cy})_2$ , indicating that it behaves as an elementary substance. It is most easily prepared by treating copper sulfate with warm potassium cyanide:

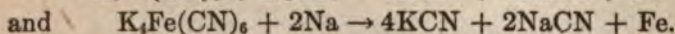
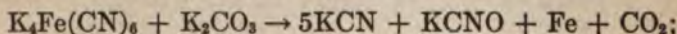


It is given the double formula because of its molecular weight. It may have either the structure  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ , or  $\text{C}=\text{N}-\text{N}=\text{C}$ . In the latter case it is a bivalent compound of carbon. Its chief importance is in its derived products, the cyanides, which are not obtained directly from it, but rather the reverse. The most important cyanides are hydrocyanic acid,  $\text{HCN}$ , also known as prussic acid, and its salts. Hydrocyanic acid is made by distillation of potassium cyanide with a less volatile acid. It is a liquid with a boiling point of  $26.5^{\circ}$  and hence at room temperature has a vapor tension almost equal to the atmospheric pressure. It has a pleasant odor, usually described as peach blossom odor, and

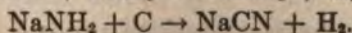
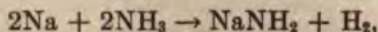
is intensely poisonous. It is an extremely feeble acid in solution and its salts, even those of the alkalies, are highly hydrolyzed. The acid probably has the structure  $\text{H}-\text{N}=\text{C}$ , and is, therefore, analogous to hydrochloric acid if we keep in mind the resemblance of the group,  $\text{CN}$ , to chlorine. This is emphasized by the formation of complex cyanides. (See cyanides of iron, copper, silver, etc.) There is considerable evidence to show that the derivatives of hydrocyanic acid may also have the structure corresponding to the formula  $\text{H}-\text{C}\equiv\text{N}$ , and that potassium cyanide in solution represents an equilibrium system of  $\text{K}-\text{C}\equiv\text{N} \rightleftharpoons \text{K}-\text{N}=\text{C}$ . Such relations as this are not infrequent in organic compounds and are fully discussed in organic texts (*q.v.*). When a substance exists in two such mutually interchangeable forms they are said to be tautomeric (*ταύτρος* = the same and *μέρος* = part). The cyanides are derived from three general sources. If calcium cyanamide (*q.v.*) is heated with a suitable flux, *e.g.*, sodium carbonate, and with carbon, the result is a molten mass of cyanide which may be brought into solution in water:



If refuse organic matter, such as horn, blood, leather scraps, etc., is heated with potassium carbonate and iron filings and the mass so formed is extracted by water (lixivation) and the solution evaporated, yellow crystals of potassium ferrocyanide, known as "yellow prussiate of potash,"  $\text{K}_4\text{Fe}(\text{CN})_6$ , are formed. This compound may be heated with potassium or sodium carbonate or with sodium or potassium. The reactions may be indicated:

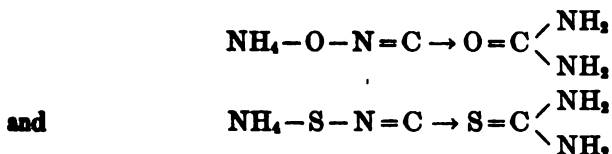


The cyanides are virulent poisons and powerful reducing agents at elevated temperatures, and show a strong tendency to form double cyanides. By reason of these properties, cyanides, particularly sodium cyanide, are manufactured on a large scale for use as germicides and in metallurgy (see gold). Sodium cyanide has almost wholly replaced potassium cyanide in metallurgical operations. It is made by heating metallic sodium with ammonia and coke. The reactions which take place are indicated by the following equations:





(See also the method of nitrogen fixation, by J. E. Bucher, Jour. Ind. and Eng. Chem., vol. 9, p. 233 (1917).) When subjected to gentle oxidation, potassium cyanide is oxidized readily to potassium cyanate,  $\text{KCNO}$ , and with sulfur is converted to sulfocyanate,  $\text{KCNS}$ . The corresponding ammonium salts are interesting because of their transformation, the cyanate on simply being allowed to stand in solution and the sulfocyanate on heating to  $170^\circ$ , into urea and sulfourea:



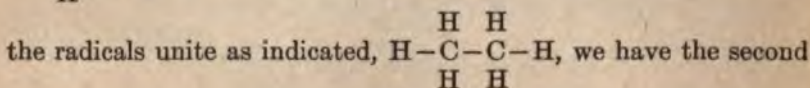
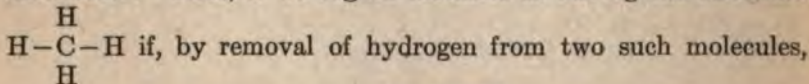
The former of these, urea, is a product of the animal metabolism, and was first prepared artificially from ammonium cyanate, in 1828, by Wöhler, by simply recrystallizing the latter. This is regarded as one of the landmarks of chemistry because it was a sort of finishing blow to the old "vitalistic" theory, which regarded the organic compounds as requiring some "vital force" for their formation. It is also an example of an intramolecular rearrangement (see p. 10), since the change consists in the structural adjustment from ammonium cyanate (see equation above), to urea.

## CHAPTER XIX

### HYDROGEN COMPOUNDS OF CARBON

**General.**—Carbon forms many hundreds of hydrogen compounds, which owe their large number to the ease with which carbon forms substances in which evidently a part of its valencies are employed in uniting with hydrogen and part in combining with other atoms of carbon (*vide infra*). These compounds are known as hydrocarbons, and they and their derivatives, numbering at present upwards of two hundred thousand, and increasing in number almost daily, are the subject matter of organic chemistry. Only a very brief outline of the subject is here attempted, as obviously any adequate treatment would require at least a special volume. The present purpose is twofold: to give the student a glimpse of the field, that "he may taste and see that it is good," and to impress the fact that this vast subject is an integral portion of general chemistry. In dealing with such vast numbers of substances, classification becomes a tremendous asset and the ease with which these substances lend themselves to comprehensive grouping has greatly facilitated their study. The hydrocarbons are grouped according to their composition into the following series: the marsh gas series of the general composition  $C_nH_{2n+2}$ ; the ethylene series  $C_nH_{2n}$ ; the acetylene series  $C_nH_{2n-2}$ ; the benzene series  $C_nH_{2n-6}$ , and certain other series of lesser present moment. These will be sufficient to illustrate the relations involved.

The simplest explanation of the possibility of the existence of these compounds is found in the hypothesis that carbon is ordinarily quadrivalent and that its atoms unite readily with each other. Thus, if we regard methane as having the structure

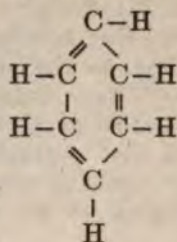




member of the series, known as ethane  $C_2H_6$ . Similarly, by repeating this union of radicals, we get  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_5H_{12}$ , etc.

In a similar manner, by removal of two hydrogen atoms and subsequent union of the radicals, we get from methane  $CH_4 - 2H \rightarrow CH_2$  and  $2CH_2 \rightarrow H_2C=CH_2$ , or ethylene, the first member of the second series. By removal of three hydrogen atoms in a similar way we get  $CH_4 - 3H \rightarrow CH$  and by combination,  $2CH \rightarrow HC \equiv CH$ , we have acetylene.

The fundamental structure of the benzene series is somewhat different in that in this series it is assumed that the carbon atoms are so connected together as to form a closed chain. This is best illustrated by the simplest compound of the fourth series mentioned above, benzene, which is believed to have the structure represented by the formula:



It would lead us too far to attempt to give the experimental bases for these assumptions, but it may be said that they are sufficient and convincing, and that their consideration is a fundamental portion of every "organic" course.

**Occurrence.** — Hydrocarbons occur in nature in large quantities and considerable variety.

Marsh gas, as the name implies, is generated in stagnant pools, or elsewhere where organic material is undergoing decomposition without free access of air. It is also found in coal mines, under pressure in pockets in the coal. When these are tapped, in mining operations, large volumes of the gas are liberated and may form an explosive mixture with the air. It is called fire damp for this reason. It is also a constant, sometimes a very large, constituent of natural gas and of the gases escaping from petroleum wells. Petroleum is a complex mixture of hydrocarbons which occurs in strata of sandstone, "oil sand," at varying depth. It some-

times issues from the earth in the form of oil springs, but is usually obtained by boring. Frequently it is found that when the oil layer is tapped, the pressure is so great that huge quantities of oil and gas are forced out in geyser-like streams. The distribution of the oil fields is very great, oil having been found first in the Baku region near the Caspian Sea. The first oil well found was that of Col. Drake near Oil City, Pennsylvania (1859), and from the development following this strike dates the modern oil-refining industry. Oil fields of greater or less magnitude are known in Pennsylvania, Ohio, Indiana, Illinois, Oklahoma, Kansas, Texas, and California, and in the Caucasus, Persia, Burmah, China, Japan, and Mexico, — to mention only a few of many localities.

The crude petroleum is a greenish brown fluorescent liquid and is usually very viscid. It contains, besides a long series of hydrocarbons, quantities of other substances which vary in character and amount according to the source. In general, there are two types of petroleum, that containing solid hydrocarbons of the marsh gas series, known as paraffins, and hence said to have a paraffin base, and that containing bitumen or asphalt. The latter type frequently contains members of the unsaturated and ring compounds analogous to the second, third and fourth series mentioned above.

The origin of petroleum is uncertain. The views are as follows: It originates from the decomposition of vegetable material under conditions of high heat and great pressure in the absence of air. This view is the source of the name "coal oil" for a portion of petroleum. It is formed by the distillation of animal matter, fish or shell fish, under like conditions. It is formed by the hydrolysis of carbides, under special conditions. It is quite possible that all three methods of formation have operated in the different fields. This is not the proper place to enter into a discussion of the validity of the evidence in favor of each.

**Distillation of Petroleum.** — When crude petroleum is heated the various components volatilize at different temperatures and while the difference of boiling point of successive members of the hydrocarbon series is not sufficient to effect complete separation, yet in general the substances of smaller molecular weight volatilize first, and by diversion of the flow of condensed materials at definite temperatures into suitable receptacles, fractions are ob-



tained which serve particular purposes. This process is known as oil refining and is the most colossal fractional distillation process carried out by man. The various fractions ordinarily produced are as follows:

Below 40°: Gases, chiefly methane,  $\text{CH}_4$ , to butane,  $\text{C}_4\text{H}_{10}$ . Used mainly in the process for fuel.

From 40° to 70°: Petroleum ether, pentane,  $\text{C}_5\text{H}_{12}$ , to hexane,  $\text{C}_6\text{H}_{14}$ . Used as a solvent and for manufacture of oil gas (*vide infra*).

From 70° to 90°: Gasoline, hexane,  $\text{C}_6\text{H}_{14}$ , to heptane,  $\text{C}_7\text{H}_{16}$ . Used as a fuel for internal combustion engines and as a cleaning agent and fuel.

From 80° to 120°: Naphtha, heptane and octane,  $\text{C}_8\text{H}_{18}$ . Uses the same in general as gasoline.

From 120° to 150°: Benzine, octane and nonane,  $\text{C}_9\text{H}_{20}$ .

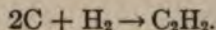
From 150° to 300°: Kerosene, decane,  $\text{C}_{10}\text{H}_{22}$ , to hexadecane,  $\text{C}_{16}\text{H}_{34}$ . Used as illuminating oil.

The still higher fractions are collectively known as lubricating oils. These, according to the temperatures at which they are distilled, deposit, on cooling, vaseline, a viscous butterlike mass, and paraffin. The lubricating oil is separated into various fractions consisting of more or less heavy hydrocarbons and adapted to the character of the bearings upon which they are to be used. The small internal friction of these oils is the reason for their use as lubricants. The vaseline is used medicinally in a great variety of ways. The paraffin is used to manufacture candles and to waterproof paper, in laundry work, and last, but not least, in the manufacture of chewing gum. The residue in the retorts is pitch and may be used in road and roof building. The process of simple distillation has to be modified somewhat in case the petroleum contains sulfur, which is ordinarily removed by distilling in the presence of cupric oxide, which is converted to cupric sulfide. The oxide can be recovered by roasting. Of course, the asphaltum base petroleum gives little or no paraffin when distilled.

The various fractions above outlined are ordinarily not suitable for immediate use for the purposes indicated and have to be further refined. For example, the kerosene fraction is treated successively with sulfuric acid, sodium hydroxide, and water in order to remove tarry material which injures its value as "lamp oil."

Natural paraffin is known as ozokerite. Asphalt, or bitumen, is also found in great natural deposits.

**Preparation.**—Hydrocarbons can be prepared by synthesis. The methods employed are varied. Two examples will serve our purpose. If electrical discharge takes place between carbon electrodes in an atmosphere of hydrogen, acetylene is formed by direct addition:



If a derivative of methane, methyl chloride, is treated with metallic sodium, the reaction,  $2\text{CH}_3\text{Cl} + 2\text{Na} \rightarrow 2\text{NaCl} + \text{C}_2\text{H}_6$ , takes place. This type of reaction serves to build up more complex hydrocarbons from derivatives of those of smaller molecular weight. Hydrocarbons are, however, if prepared artificially, ordinarily made by decomposition of more complex compounds formed in nature, or of compounds which are made for the purpose. Three examples will be given.

**Distillation of Wood.**—When wood is heated in closed retorts until decomposition takes place (destructive distillation) the products vary somewhat according to the temperature employed and the material used, but in general four products are obtained: (1) Gas, mainly methane; (2) an aqueous solution containing as its chief components wood alcohol, acetone and acetic acid; (3) a viscous black mass known as tar, from which, by separate distillation, a great variety of hydrocarbon oils can be obtained; among them in most cases turpentine  $\text{C}_{10}\text{H}_{16}$ ; (4) a residue of charcoal.

**Distillation of Coal.**—When bituminous coal is distilled in closed retorts the result is the formation of the same four types of

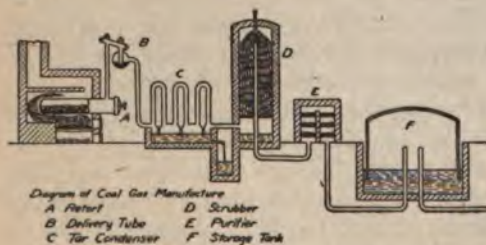


Fig. 85.

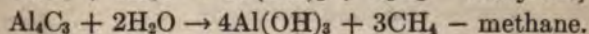
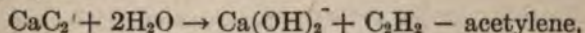
product as with wood. (Fig. 85.) The gas, however, contains, along with methane, large quantities of hydrogen and some carbon monoxide, as well as small quantities of other hydrocarbons. (See illuminating gas.) The tar, coal tar, on distilla-

tion, reveals itself as a veritable mine of compounds of the hydrocarbon type, which in recent years have most wonderfully served mankind as a source of medicine for his ills, dyes for his enjoyment,



poisons for his enemies of the insect world, and explosives for his great guns. The miracle of coal tar and its products is, alas, not to be told in this place, but its telling forms a most attractive chapter in organic chemistry. Among the hydrocarbons derived from it are benzene or benzol,  $C_6H_6$ , naphthalene,  $C_{10}H_8$ , familiar as moth balls, but vastly useful otherwise as well, and anthracene,  $C_{14}H_{10}$ .

**Hydrolysis of Carbides.**—When carbides are treated with water or acids, decomposition takes place as indicated by the following equations:



Other carbides react in a similar manner and produce various hydrocarbons.

**Properties.**—The properties of the hydrocarbons are so varied that it is difficult to discuss them without taking up individual examples. A few general statements concerning each series may be made.

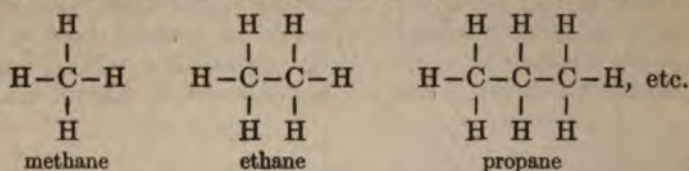
The smaller the molecular weight of the members of each series, the more volatile they are. This may be illustrated by the following table, which gives the formulæ and boiling points of a few of the simpler members of three series.

The methane series.	The ethylene series.	The acetylene series.
$CH_4$ $-160^\circ$		
$C_2H_6$ $-93^\circ$	$C_2H_4$ $-105^\circ$	$C_2H_2$ $-83.6^\circ$
$C_3H_8$ $-45^\circ$	$C_3H_6$ $-40^\circ$	$C_3H_4$ $-23.5^\circ$
$C_4H_{10}$ $1^\circ$	$C_4H_8$ $1^\circ$	$C_4H_6$ $27^\circ$
$C_5H_{12}$ $38^\circ$	$C_5H_{10}$ $39^\circ$	$C_5H_8$ $48^\circ$
$C_6H_{14}$ $70^\circ$	$C_6H_{12}$ $69^\circ$	$C_6H_{10}$ $80^\circ$

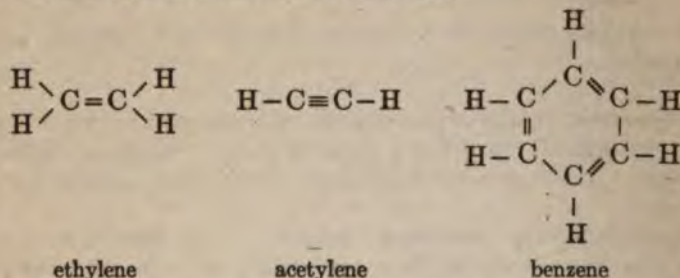
In the methane series, at room temperature, all the members below pentane ( $C_5H_{12}$ ) are gaseous, those below pentadecane,  $C_{15}H_{32}$ , are liquid, and those more complex are solid. In each series above given it will be noted that the successive members differ from one another by a constant quantity,  $CH_2$ . Such series are known as homologous series.

The first series is known not only as the methane series, but also as the saturated series and as the paraffin series (*parum* = little and *affinis* = affinity). The latter names indicate the relative chem-

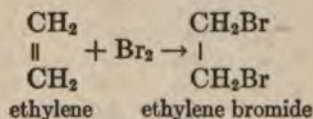
ical inactivity of the members of the series. This is to be expected if the graphic formulæ below correctly represent the structure:



If four is the maximum valency of carbon then only by substitution or decomposition can derivatives be made. On the other hand, if the other series present carbon atoms which are linked to each other by more than one bond, *e.g.*,



then by addition of elements or radicals the saturated derivatives may be obtained, *i.e.*, the "double" or "triple" bonds may be converted to single bonds. Thus:



In general, then, the members of the unsaturated series may undergo change by addition, as well as by substitution and decomposition.

The hydrocarbons are also capable of presenting themselves, or of being prepared, in polymeric forms. These are of two types. Two hydrocarbons may have the same percentage composition and yet possess different molecular weights and with this difference present very different properties, *e.g.*, benzene,  $\text{C}_6\text{H}_6$ , and acetylene,  $\text{C}_2\text{H}_2$ . Such compounds are said to be metamers, or



simply polymers. The second type appears when substances have the same percentage composition, the same molecular weight and yet are different. These are known as *isomers* or as isomeric forms. Thus we have two substances of the formula  $C_4H_{10}$ . The explanation of their existence and of their differences in properties is found in structural formulæ. Thus in the case cited, we represent one by the formula  $CH_3CH_2CH_2CH_3$  and the other by  $\begin{matrix} CH_3 \\ \diagdown \\ CH \cdot CH_3 \\ \diagup \\ CH_3 \end{matrix}$  and believe that in the difference of radicals and of arrangement lies the cause of their difference of properties. (See stereo formulæ.) In these and similar formulæ we find an explanation of the exceedingly great numbers of hydrocarbons and their derivatives.

All hydrocarbons burn more or less readily and the ultimate products of their combustion are carbon dioxide and water. This property determines their extensive use as fuels, both as gases and as liquids (see fuel gases and liquid fuels). The fact that in so burning they in most cases furnish white light also extends their usefulness (see flame). When the hydrocarbons are mixed with oxygen or air in proper proportions and are ignited, the rate of combination and the heat produced are sufficient to produce explosion, and these explosions may be so controlled as to be utilized for motive power (see explosive mixtures).

When the hydrocarbons of large molecular weight are heated suddenly, they tend to decompose, giving free carbon and hydrocarbons of lesser molecular weight. This process is known as "cracking" and in the process of fractional distillation is accomplished by allowing the less volatile constituents to condense and fall into the highly heated residue in the retorts. The method has recently come into extensive use because the demand for lighter hydrocarbons, as compared with the heavier, is greater than the relative proportions found in petroleum or in the products of wood and coal distillation. (See also Rittman's Process, Journal of Industrial and Engineering Chemistry, vol. 7.)

Perhaps the most important property of the hydrocarbons is the extent and ease of substitution, directly or indirectly accomplished, of hydrogen by other elements and radicals. The importance of this will be made more manifest when the derivatives are discussed. (See Chap. XX.) The brief outline of properties here presented is only intended to convey an impression of the possibilities of reaction and is not intended as a complete presentation.

**Uses.**—The uses of the hydrocarbons, as has already been intimated, are extensive and varied. In addition to their use as raw material to produce derivatives (see Chap. XX), they find direct application in many ways, but especially as fuel, as illuminants, and as explosives. We may, then, with profit, limit our discussion to these three phases and treat them under the headings: Illuminating and Fuel Gases; Flame and Explosive Mixtures.

**Illuminating and Fuel Gases.**—For the most part the materials of gaseous type used as light- or heat-producing media are mixtures, more or less complex according to their source. The following table will present the more important varieties and a typical analysis of each. The table will be followed by comments upon some of them.

Type of gas.	Hydrogen, per cent.	Methane, per cent.	Heavy hydrocarbons, per cent.	Carbon monoxide, per cent.	Carbon dioxide, per cent.	Nitrogen, per cent.	Oxygen, per cent.
Natural gas.....	2.2	92.6	0.5	0.5	0.3	3.6	0.3
Coal gas.....	49.0	34.5	5.0	7.2	1.1	3.2	0.0
Water gas.....	46.3	1.3	0.0	45.6	2.1	4.2	0.1
Carburetted water gas.....	40.2	16.8	8.7	28.7	1.2	4.3	0.1
Producer gas.....	8.6	2.0	0.4	24.4	5.2	59.3	0.1
Blast furnace gas.....	2.7	0.2	....	28.6	11.4	57.1	....
Oil gas.....	....	38.8	60.1	....	....	1.1	....

As will be seen from the table, with the exception of natural gas and oil gas, the hydrocarbons do not form a large quantity factor in the composition of commercially used gases, yet the discussion of them comes properly under this head because, first, the illuminating value of these gases rests upon their hydrocarbon content, and, second, the process by which they are obtained involves carbon or its hydrocarbon derivatives, and, third, because we are only now in possession of general chemical information concerning all their component factors.

In each case, the student must realize that the composition given in the table is only that of a representative sample. Thus natural gas may be nearly all methane, as indicated, or it may be, as in that from the famous Delamater well near Pittsburgh, nearly pure ethane. Similar variations of composition, according to their source, occur with the other types of gas.

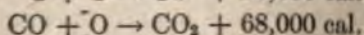
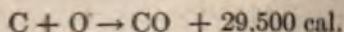


Coal gas, made by the distillation of coal, varies in composition not only with the coal used, but also with the temperature at which the distillation is carried out. It is the type of gas most used in Europe for city gas supplies. In the United States, carbureted water gas, or mixed water gas, is made by passing steam over highly heated coal or coke and the reaction,



produces, therefore, essentially only carbon monoxide and hydrogen (water gas). Such gas, while cheaply produced, is non-luminous when burned and is, moreover, of relatively low calorific value. If, however, crude petroleum is "cracked" by being passed over highly heated "checker work," it produces gases which do not liquefy when cooled, — mainly ethylene and its homologues — and these impart illuminating value to the flame. (See flame.) These gases, mixed with water gas, give the carbureted water gas.

Producer gas is, so far as its heat-producing factor is concerned, essentially carbon monoxide, and is made by passing a limited stream of air over highly heated coal or coke. The means employed to effect this are extensively varied and for details the student is referred to works on engineering and industrial chemistry. The carbon monoxide so produced is not, of course, capable of producing by its combustion so much heat as the original coal or coke. But by reason of superior efficiency gained by use of a gaseous fuel, a greater proportion of the total heat production of burning carbon may be utilized by first wasting approximately 30 per cent of the total fuel value.



In the iron industry, as well as in other smelting processes, large quantities of producer gas are obtained incident to the normal operation of the process and in recent years vast quantities of this gas are employed for heat production and in internal combustion engines.

Oil gas is a general term applied to gaseous mixtures of the vapor of gasoline and air, or to gaseous mixtures produced by cracking crude petroleum in hot retorts. The latter type is the one given in the table. In this country it is used chiefly for lighting ~~trains~~ under the name of Pintsch gas. Besides these gaseous ~~mixtures~~

acetylene is of recent years finding extensive use for automobile lighting and for country homes. It is made from calcium carbide and used as prepared.

**Flame.** — Some difficulty is encountered when we attempt a comprehensive definition of the term flame, but, in general, we use the term to describe the phenomena which accompany the rapid union of gases. The term is usually limited to those cases where explosion does not occur and where heat, always, and light, usually, are produced.

In order to produce a flame, it is necessary to bring a "combustible gas" heated to its kindling temperature into contact with a "supporter of combustion." This is most easily realized in air by allowing a stream of gas to issue from a suitable opening, and by means of a match, taper, or electric spark initiate combustion. In such a case, the air is considered as a supporter of combustion and the issuing gas as combustible. These terms are merely conventional, as the action is mutual on the part of the gases. Were the atmosphere hydrogen or illuminating gas and a jet of oxygen were introduced under like conditions, a flame would be produced and we would regard the oxygen as combustible. This condition is illustrated by burning a jet of air in illuminating gas.

Probably the most familiar flames are those produced by burning wood, coal or other fuel in free contact with air. The gas in such cases is produced by the heat of combustion of the fuel and the rate of production is usually regulated by control of the access of the air to the fuel. The gases we have been considering are usually prepared in anticipation of their use and the rate of combustion regulated by the rate of flow of the gas which is, in turn, governed by the pressure under which it is kept in the gas holders, or mains, and the size of the openings through which it flows. The usual device for securing proper contact of air and the other gas is some modification of the Bunsen burner. This instrument has two essential parts: A tip from which the gas issues, and a larger tube in which the gas is mixed with the air. The air may enter the larger tube through openings at its base, as in the laboratory device. In the larger burners used to heat boilers, the tube consists only of the circular opening in the furnace base and the air comes in contact with the gas only at the outer burning surface of the jet.

The ordinary burner flame may be either "luminous" or "non-luminous." In the latter case, all or nearly all, the chemical energy



of the reacting gas is converted into heat. In the former, a part appears as light energy. It is evident that since either light or heat may be sought as the object of gas consumption, the conditions determining the ratio of heat to light production are at times of great moment. Some gases burn only with practically a non-luminous flame, *e.g.*, hydrogen, carbon monoxide, methane, etc. If it is desirable to utilize such gases as sources of light, the result may be attained by mixing the gas with varying quantities of gases, or very volatile liquids, which burn with luminous flames. This is in part the object sought and attained by using petroleum in the manufacture of "enriched" water gas. (The calorific value of the gas is also so increased.) Other gases burn with luminous flames of greater or less intensity. Examples of such are acetylene and ethylene, phosphorus vapor, etc. The cause of the luminosity of such flames has been the subject of much investigation and many hypotheses. For a very full and satisfactory discussion see Mellor's *Modern Inorganic Chemistry* (pp. 733-761). The general conclusion is that in different gases the luminosity is due to different causes, yet in the burning hydrocarbon gases it appears that the most satisfying view is as follows: The heat of the burning gas converts a portion of the unburned heavier hydrocarbons to acetylene. The latter is an endothermic compound and at the moment of its dissociation by the heat of the flame the carbon particles freed are by the heat of dissociation rendered incandescent.

The Bunsen luminous flame may be made less luminous by mixing air with the gas before it issues from the burner by means of the openings at the base of the tube. The rising current of gas draws in air and the result is a concentration of the volume of the flame and a consequent higher temperature. That this increased temperature is not the sole cause of non-luminosity is clear from the fact that the same result, at lower temperature, may be secured by admitting nitrogen or carbon dioxide in lieu of air.

The production of gases which give luminous flames is at present of little importance because of the use of the Welsbach mantle. This consists of a gauze of cerium and thorium oxides which, when heated in a Bunsen flame, glow with a brightness much more intense than that of the gas which heats them. Hence the candle power of gas is of much less importance than its calorific value.

The calorific value of a gas is usually expressed in the quantity of British thermal units per cubic foot of gas burned and in many

states gas companies are compelled by law, or by the public service commissions, to keep their product up to a certain calorific standard. The *temperature* of a burning gas is vastly modified by the manner and the rate of burning. Thus in the ordinary burner of the Bunsen type, using coal gas, the maximum temperature attainable, even with open base holes, is about  $1500^{\circ}\text{C}$ ,

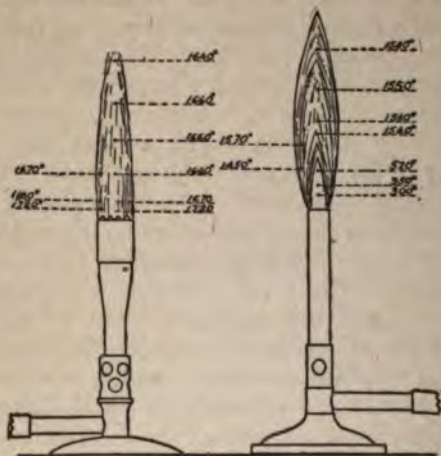


FIG. 86.

while with a burner of the Meker type, a maximum temperature of nearly  $1800^{\circ}$  can be attained. (Fig. 86.) This difference of temperature is secured by burning an increased quantity of gas in smaller volume by more intimate mixing with air. By means of the blast lamp or blow pipe still higher temperatures may be reached, but the principle involved is the same.

**Explosive Mixtures.**—When gases capable of burning with each other are mixed in proper proportions and ignited the same reaction goes on as when one is burned from a jet in an atmosphere of the other, but when the heat of reaction of the portion first ignited is sufficient to maintain the kindling temperature of the adjacent mixture the reaction rapidly proceeds as a sort of “wave” through the whole volume of mixed gases at a rate which depends upon the type of mixture. If the walls of the containing vessel are not sufficiently strong to stand the pressure incident upon the increase of temperature of the resulting gaseous products



(or perhaps increased volume), we have an "explosion." An explosion may be defined without serious error, as a sudden increase of gaseous volume. Of course, if the proportion of either gas is not sufficiently great, by its combustion, to raise the adjacent mixture to the kindling point, or if the combination is endothermic, no explosion results. Thus, with air and various gases, the maximum and minimum ratios for an explosive mixture are approximately (see Mellor, p. 742) as given in the following table:

	Minimum.	Maximum.
Acetylene.....	3 parts per 100	52 parts per 100
Ethylene.....	4 parts per 100	15 parts per 100
Marsh Gas.....	6 parts per 100	13 parts per 100
Coal Gas.....	8 parts per 100	19 parts per 100
Water Gas.....	12 parts per 100	67 parts per 100
Hydrogen.....	9.5 parts per 100	65 parts per 100
Carbon Monoxide.....	16.5 parts per 100	75 parts per 100

Of course, if the vessel be strong enough to stand the strain, no actual explosion can take place, but the "explosion wave" will traverse an explosive mixture and, indeed, attain a maximum speed, which is constant for a given mixture of gases. It is also apparent on consideration that a proper mixture of gases not confined in a vessel may explode when ignited, *i.e.*, the sudden expansion of gas may take place against atmospheric pressure only.

Other combustible mixtures, such as coal dust or flour dust and air, may also explode violently. The principles involved are the same as those above given.

**Fuels.** — Fuels may be considered roughly as of two types, solid and gaseous. While, of course, many fuel substances are liquid, yet when used as fuel they are first converted to gaseous form. This is, indeed, also true of certain solid fuels as tallow, paraffin, spermaceti, etc. Thus, when crude petroleum, kerosene, or gasoline are burned, the process consists essentially in a controlled conversion of the liquids into gaseous form and their subsequent combustion as near to the seat of operation as possible. This conversion to gaseous form is, of course, very easy in the case of the volatile liquid gasoline, and the explosive mixture method of utilization is used in the internal combustion motors. In the case of the less volatile crude petroleum the volatilization of the

liquid is facilitated by spraying by means of a steam jet (see Fig. 87).



FIG. 87.

Under certain circumstances it is impossible to utilize the heat of solid fuels without great loss and hence for certain purposes it is advantageous to convert coal to producer gas, even at great loss of heat, in order by better adjustment of heat source to object, to utilize a larger percentage of total heat. In other circumstances, solid fuels may be of definite advantage, *e.g.*, aluminium in the thermite reduction process (see Goldschmidt process).

The economic utilization of fuels and the adaptation of fuel to purpose forms a very large and important chapter in Industrial Chemistry and knowledge of the subject is an essential in the equipment of the chemical engineer.



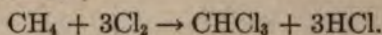
## CHAPTER XX

### DERIVATIVES OF THE HYDROCARBONS

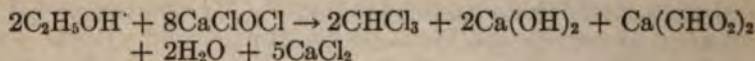
IN order to gain a comprehensive view of the vast group of substances included under the heading of this chapter, it will be necessary to outline the types of compounds and present illustrative examples of each. Perhaps the simplest plan is to take them up under the general head: Halogen derivatives, oxygen derivatives, nitrogen derivatives, etc., and consider the subdivisions of each head. In making such an attempt at systematization, we shall encounter the usual difficulties of classification and find compounds of mixed types.

**Halogen Derivatives.** — When discussing chlorine, attention was called to the fact that one of its chemical properties is the facility with which it may be made to take the place of hydrogen in organic compounds (p. 121). Thus, if methane be treated with chlorine, the displacement of hydrogen may be made to pass through successive steps to produce methyl chloride,  $\text{CH}_3\text{Cl}$ , methylene chloride,  $\text{CH}_2\text{Cl}_2$ , chloroform,  $\text{CHCl}_3$ , and finally by complete substitution, carbon tetrachloride,  $\text{CCl}_4$  (p. 121). Similar compounds are produced by reaction between all the hydrocarbons of the methane series and any of the halogens. The other hydrocarbon series may produce halogen derivatives by substitution and, since they are unsaturated, also by addition. For example, it is possible to produce from benzene,  $\text{C}_6\text{H}_6$ , not only such compounds as  $\text{C}_6\text{H}_5\text{Cl}$  and  $\text{C}_6\text{H}_4\text{Cl}_2$  but also benzene hexachloride,  $\text{C}_6\text{H}_6\text{Cl}_6$ , etc. Substitution is further complicated by the existence of isomers. We have, for example, two dichlor derivatives of ethane,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$  and  $\text{CH}_3\text{CHCl}_2$ , known as ethylene dichloride and ethylidene chloride. Also there are three isomeric disubstitution products of benzene, known as the ortho-, meta-, and para-derivatives. It will be evident, then, that the halogen derivatives are very numerous. Two of them may be very briefly discussed to illustrate the type.

Chloroform,  $\text{CHCl}_3$ , may be made by direct treatment of methane with chlorine,



The reaction takes place only in the sunlight and is slow. The other substitution products are formed at the same time. If, however, alcohol and bleaching powder are allowed to react upon each other in solution, a reaction takes place which may be indicated,



though it is in reality a more complex reaction. Also chloroform may be, and usually is, made from acetone (*q.v.*). Similarly, the other halogen derivatives may be made not alone by substitution, but also by starting with compounds of various types, themselves derivatives of hydrocarbons.

Chloroform is a colorless, sweet-smelling liquid of specific gravity 1.526 and boiling point  $61.2^\circ$ . Its vapor when inhaled produces anæsthesia. The use of it in surgery was introduced by Simpson in 1848, and since then countless lives have been prolonged by the use of it and other anæsthetics in operations otherwise impossible, and infinite human pain has been spared. Other anæsthetics have largely usurped its place in surgery because of the occasional fatal results in its use, but to ease the pain of childbirth no other has the same value, though recently scopolamine has been used to induce the so-called "twilight sleep," the success of which is still an open question.

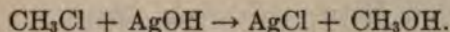
Iodoform,  $\text{CHI}_3$ , a solid substance of pronounced odor, is made by treatment of alcohol with iodine in the presence of an alkaline substance. It is a powerful germicide much used in dressing wounds. Like chloroform, its importance is less at present than formerly, by reason of the extensive use of other substances.

**Oxygen Derivatives.** — These derivatives are of tremendous variety. They may be considered under the following heads:

**Alcohols and Phenols.** — If in a hydrocarbon molecule, we introduce the hydroxyl group in place of a hydrogen atom, we obtain an "alcohol," if the hydrocarbon is of the "chain" type, or a "phenol" if of the benzene series. This result is accom-



plished if we treat a halogen derivative of the hydrocarbon with a weak base, *e.g.*,



There are numerous methods by which alcohols are produced from more complex compounds. Of these, it is perhaps sufficient to mention three:

First, the fermentation of sugar or of sugar-like substances. This decomposition is carried out on an enormous scale in the manufacture of ordinary alcohol (*q.v.*).

Second, the saponification of fats (*q.v.*). This likewise is an industrial process of first rank.

Third, destructive distillation of wood, or of its metamorphosed form, coal. This method is of industrial importance especially in the production of wood alcohol,  $\text{CH}_3\text{OH}$ , and of phenol and its homologues.

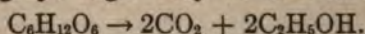
The alcohols are characterized by their possession of the hydroxyl group without marked acidic or basic properties, though with acids they react under special conditions, slowly, to produce water and a class of salts known as esters of which the fats are examples. They also can be made to yield hydrogen, when treated with the active metals, and produce alcoholates. They are non-conductors of electricity and in aqueous solution give nearly "normal" freezing and boiling-point values.

The phenols are more markedly acidic than basic, though still amphoteric, and are readily affected by oxidizing agents.

The alcohols of the lower hydrocarbons are also markedly narcotic substances, *i.e.*, they diminish the control of the mind over the nervous system and are consequently intoxicants. The phenols are specially powerful germicides, and find their most extensive direct use as such.

There are several varieties of both alcohols and phenols. Thus, we have alcohols containing only one hydroxyl group per molecule (monohydric alcohols), of which the best known examples are wood alcohol,  $\text{CH}_3\text{OH}$ , and grain alcohol,  $\text{C}_2\text{H}_5\text{OH}$ . Also alcohols may have two, three, four, or more hydroxyl groups per molecule. For example, we have glycol,  $\text{C}_2\text{H}_4(\text{OH})_2$ , glycerine,  $\text{C}_3\text{H}_5(\text{OH})_3$ , etc. These are collectively known as polyhydric alcohols. Similarly, we may have mono-, di-, or trihydroxyphenols.

Ordinary alcohol will be used to illustrate the group. Its production from grape sugar may be formulated:

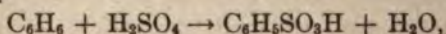


This reaction takes place when the sugar is present in aqueous solution with yeast. Yeast is a type of plant which has been shown to secrete a substance, zymase, capable of acting as a catalytic agent in facilitating the production of alcohol. The process is known as fermentation and takes place not only with glucose, or grape sugar, but also with cane sugar and starch and even with cellulose, if these substances are subjected to hydrolysis previous to or during the progress of the fermentation. Alcohol is, then, one of the products of "leavened" bread, though the leavening is due to the carbon dioxide simultaneously produced (see also sugars).

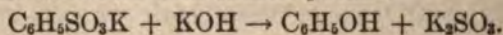
The alcohol so produced is also known as "grain alcohol" and as "spirits of wine" and as "alcohol." The last name indicates its predominant importance among its homologues.

The uses to which alcohol is put indicate in a general way its characteristics. It is used as a fuel, since it burns with a non-luminous flame, and has high calorific value. It is also used as a solvent of gums, resins, flavors, etc. It is a most excellent solvent. It is used to manufacture ether (*q.v.*) and acetic acid (*q.v.*). It is also used in beverages; whiskey, rum, wine, and beer, in all their numberless modifications, are essentially more or less dilute solutions of alcohol. While these beverages differ from each other in flavor, food content, method of manufacture, etc., they all owe their extended use and abuse to their alcohol content, which varies from 3 to 4% in the milder beers and wines to 50 to 60% in the strongest liquors. The necessity of careful control of this, the intoxicating property of alcohol, interferes sadly with its varied and extensive uses in other ways (see Bunge's *Physiological Chemistry*, Chapter IX).

Ordinary phenol, also known as carbolic acid, is the most important member of its class. It is one of the important substances derived from coal tar, which is its principal source. It may be prepared from benzene by first converting the latter to a sulfonic acid.



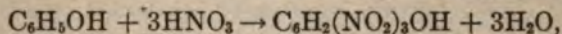
and fusing the sulfonate with caustic potash:





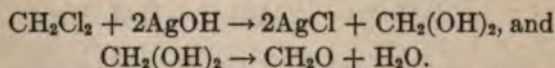
The fused mass may be acidified with sulfuric acid and the phenol extracted with ether.

Phenol is an active poison, not only for small protoplasmic organisms, but for higher organisms as well. In both cases the destructive effect is due to coagulation of the albumin, and the carbolic acid "burns" are due to coagulation and not to disinfection. It is a very weak acid. Aside from its use, and abuse, as a poison, phenol finds extensive application by reason of the ease with which it reacts with other substances to produce further substitution in the benzene ring. This may be illustrated by its behavior with concentrated nitric acid to produce picric acid,



which is an extensively used explosive.

**The Aldehydes.** — When the attempt is made to produce derivatives of methane containing two hydroxyl groups attached to one carbon atom, we get, instead, a type of compound which is known as aldehyde. Thus:



The compound so produced,  $\text{CH}_2\text{O}$ , formaldehyde, is the simplest as well as the best known representative of the group. Its synthesis

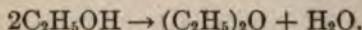
indicates the structure  $\text{H}-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}$ , and we may represent the group by the general formula  $\text{R} \cdot \text{CHO}$  where R is any radical.

While the aldehydes *may* be prepared as indicated, the usual process is to produce them from more complex compounds by decomposition or reduction. Formaldehyde gets its name from the fact that it may be produced by reduction of formic acid. It is a gas of marked and unpleasant odor. It dissolves readily in water and the 40 per cent solution is the commercial form. The substance has several points of special interest. It is perhaps the most extensively used of all gaseous disinfectants and is especially frequently employed in house disinfection. It undergoes polymerization readily to produce a solid modification  $(\text{CH}_2\text{O})_3$ , and ultimately a sugar,  $\text{C}_6\text{H}_{12}\text{O}_6$ , similar to grape sugar. Its formation is most probably the first step in the synthesis of sugar, starch and cellulose in the process of plant growth.



This process is endothermic and sunlight furnishes the required energy and chlorophyll, the green material of leaves, the necessary catalytic agent. The general property of the aldehydes, ease of oxidation, is illustrated by the common method of disinfection, in which potassium permanganate, an oxidizing agent, is added to the aldehyde and the heat of reaction with a part of the aldehyde drives the remainder out of solution as a gas. The best known aldehyde of the ring type is benzaldehyde,  $C_6H_5 \cdot CHO$ , known as oil of bitter almonds. This aldehyde has an important place in the history of organic chemistry. (See Schorlemmer's *Rise of Organic Chemistry*.)

**Ethers.** — When alcohols are treated with appropriate dehydrating reagents, water is eliminated from two molecules of the alcohol and bodies are produced which bear the same relation to alcohols as the inorganic oxides to the corresponding hydroxides. Thus we have from ordinary alcohol by use of sulfuric acid as a dehydrating agent,



The ethers may be represented by the general formula  $R-O-R^1$  and  $R^1$  may or may not be the same radical as  $R$ .

Of the ethers the most valuable is "sulfuric ether,"  $(C_2H_5)_2O$ , so-called because of the use of sulfuric acid in its manufacture. It is a very volatile liquid (b.p.  $34.6^\circ$ ), and owes its value to this volatility coupled with its power of producing anæsthesia. It is also extensively used as a solvent, particularly for fats and oils.

**The Acids.** — The organic acids form a very large and important group of compounds. The group characteristic of them is called the carboxyl group  $-COOH$  and may be considered as derived from the hydrocarbons by the introduction of three hydroxyl groups in place of three hydrogen atoms with subsequent elimination of water. Thus methane,  $CH_4 \rightarrow HC(OH)_3 \rightarrow HC \begin{smallmatrix} \nearrow O \\ \searrow OH \end{smallmatrix}$ , formic

acid. There is a very great variety of such compounds. There is possible a series of acids containing one, two, three, or more carboxyl groups corresponding to each hydrocarbon series. We may then represent the general formula of the monobasic acids by the formula  $R-COOH$  where  $R$  is a univalent radical and the other



series by  $R^1 \cdot (\text{COOH})_x$  where  $x$  has a value dependent upon the valence of  $R^1$ .

The series of monobasic acids derived from the methane hydrocarbons are known as the fatty acid series because organic salts of certain of the more complex members are the ordinary fats. Indeed many of the acids occur either as salts or as free acids in nature.

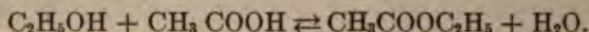
Acetic acid,  $\text{CH}_3\text{COOH}$ , the second member of the series, is made by direct oxidation of ordinary alcohol, but the progress of the reaction is difficult to control since too vigorous reaction produces carbon dioxide and water. With the aid of the bacterium, *Mycodermus acetis*, colonies of which are known as "mother of vinegar," the oxidation takes place in the air at the ordinary temperature in alcoholic solutions of not too great concentration. The product is known as vinegar. Its acid content is usually about 4 per cent. It contains besides water and the acid the flavoring materials and salts of the fruit juices from which the alcohol was prepared. From vinegar by fractional distillation a very concentrated acid may be prepared, and when this is cooled sufficiently, pure acetic acid may be frozen out. The pure acid is known as "glacial" acetic acid. It boils at  $118^\circ$  and melts at  $16.7^\circ$ .

Acetic acid is also formed when wood is distilled and the aqueous solution, pyroligneous acid, may be used as a source of artificial vinegar or of pure acetic acid. The greater portion of the acid obtained from wood is converted into acetate of lime and used for the preparation of acetone. (For additional points concerning this series of acids, see fats.)

Of the dibasic acids of the paraffin series, the simplest member, oxalic acid, is regarded as composed of two carboxyl groups,  $\text{HOOC}-\text{COOH}$ . Its salts are of frequent occurrence in nature, especially its acid salts in the different varieties of oxalis. It is a crystalline substance,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , which finds extensive use as a laboratory reagent. Its calcium salt is the most insoluble salt of calcium and is hence used in the quantitative determination of the metal. It is also an excellent reducing agent.

The acids containing several carboxyl groups, the polybasic acids, are not of great importance, but certain "mixed acids" are and will be referred to later. (*Vide infra.*) The most important of the acids of the ring type is benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , and while found in nature in certain fruits, *e.g.*, in cranberries, is made ordinarily from coal tar. It is used in various ways, the best known being as a preservative of beverages and food materials.

**Esters.** — The salts of organic acids made by replacement of the hydrogen of the carboxyl group by an organic radical are known as esters, or as ethereal salts, *e.g.*:



The direct formation of these compounds is slow owing to the weakness of the alcohols as basic substances and to the small ionization in general of organic acids. The reaction is also reversible and hence is made more complete in the direction  $\rightarrow$  by the presence of dehydrating agents. The ethereal salts differ from ordinary inorganic salts in being not only more uniformly insoluble in water, but in being non-electrolytes even when soluble. The name ester was coined to emphasize this difference. The name ester is also used for the salts produced by reaction between inorganic acids and alcohols. Certain of these have been already mentioned in connection with nitric acid (*q.v.*).

The esters of certain acids are present in fruits and flowers, and either singly or as mixtures are responsible for most of the flavors. The esters of the monohydric alcohols with the more complex acids of the paraffin series are known as *waxes*. The glycérine salts of the higher acids of the same series are known as *fats*.

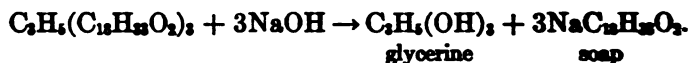
**Fats.** — Of the fats, the most important are the glycerides of palmitic acid ( $\text{C}_{16}\text{H}_{32}\text{O}_2$ ), of stearic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ), and of oleic acid ( $\text{C}_{18}\text{H}_{32}\text{O}_2$ ). These mixed with each other in varying proportions and with small quantities of other esters make up the fats, such as lard, tallow, suet, etc.

Olein,  $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{31}\text{O}_2)_3$ , is the glyceride of an unsaturated acid of the ethylene series and is the most common of the *liquid fats* which are known as *oils*. These oils very frequently occur in seeds and sometimes contain esters of unsaturated acids, such that, when exposed to the air, they oxidize to solid forms and hence may be used in paints and varnishes as dryers, or frequently as varnishes. Examples are linseed oil, hemp oil, china wood oil, etc.

In other cases, the oils will not harden on exposure to the air, but by conversion of the unsaturated radicals to saturated by addition of hydrogen, solid fats similar to animal fats may be prepared. An example is cottonseed oil, which by hydrogenation, using finely divided nickel as a catalytic agent, is converted into "Crisco," an edible fat.



**Saponification: Soaps.** — The reversal of the reaction mentioned on p. 362 is favored, of course, by increase of concentration of hydroxyl ions, and if alkali hydroxides are used, the products when fats are used are glycerine and a soap. The process is, therefore, called saponification. Thus:



The solid soaps are the sodium salts of the fatty acids, while soft soaps are potassium salts.

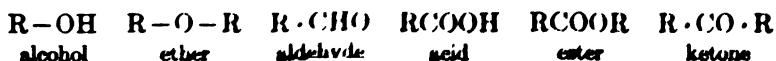
The soaps produced from the various natural fats differ somewhat according to the composition of the fat used and also vary in respect to the amount of glycerine which is allowed to remain in the soap. The soaps also are varied in character by admixture of abrasive material, such as sand, tripolite, volcanic ash, etc., or of medicinal or odoriferous substances. The soaps vary, too, in water content, and certain varieties are mixed with air to make the specific gravity of the cake less than that of water.

Soaps are the salts of weak acids with strong bases, and when dissolved in water are alkaline in reaction. Their cleansing power depends in part upon this alkalinity in solution and in part upon the increase of surface tension. They soften hard water by conversion of the soluble salts of calcium and magnesium into insoluble soaps of these metals.

**Ketones.** — When calcium acetate is distilled, a substance known as acetone is produced,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \rightarrow \text{CaCO}_3 + (\text{CH}_3)_2\text{CO}$ . This is the simplest representative of the type of compound known as ketones of the general formula  $\begin{matrix} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R} \end{matrix} (\text{O})$ . Acetone itself finds

large use as a solvent and for the preparation of chloroform, but the chief interest of the group for us in the present connection is in their relation to sugars (*q.v.*).

**Mixed Compounds.** — The relations of the oxygen compounds may now be profitably summarized by a rehearsal of the general formulæ as follows:



It should now be apparent, in view of the general character of organic relations, that it is perfectly possible that compounds are known in which more than one of the above characteristic relations occur in a single substance. Such compounds occur in nature, and are also synthesized in great numbers and in large quantities. We shall illustrate them by two types, the carbohydrates and the alcohol acids.

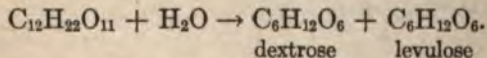
**Carbohydrate** is a term used to describe a closely related group of substances, which includes: the simple sugars, the complex sugars, starch and cellulose. They have in common that the proportion of hydrogen to oxygen in them is the same as in water. The sugars are soluble in water, while starch and cellulose are not. The simple sugars which are best known are those having the composition expressed by the formula  $C_6H_{12}O_6$ . The most familiar of these are dextrose, also known as glucose and as grape sugar, and levulose, known also as fructose and as fruit sugar. The former is a substance which contains five hydroxyl groups and one aldehyde group. The latter has a ketone structure. The relation may be indicated by the structural formulæ:

Glucose,  $CH_2OH-CHOH-CHOH-CHOH-CHOH-CHO$ .

Fructose,  $CH_2OH-CHOH-CHOH-CHOH-CO-CH_2OH$ .

These sugars both occur in many varieties of fruits and usually in unequal quantities. In honey, both are present in practically equal quantities. Their most striking difference in properties is that dextrose rotates the plane of polarization of light to the right, and levulose to the left. (For explanation of this physical property see any text-book on organic chemistry.)

The sugar found in sugar cane, in beets and in the sap of the maple tree has the composition  $C_{12}H_{22}O_{11}$ , and when treated with dilute acids, dilute alkalis, or with certain enzymes, it simultaneously takes up one molecule of water and breaks down into dextrose and levulose:



The process is slow and the acid, alkali, or enzyme is to be considered as a catalyzer and the decomposition as hydrolysis. A similar though not identical hydrolysis of starch and of cellulose produces from them simple sugars. Starch and cellulose both have a composition expressed by the empirical formula  $C_6H_{10}O_5$ ,



but while the molecular formulæ of neither are known, they are certainly different, and we ordinarily express them by  $(C_6H_{10}O_5)_x$  and  $(C_6H_{10}O_5)_y$ , where  $x$  and  $y$  are certainly very large numbers. The term cellulose covers a large variety of different substances, of similar properties, such as make up the framework of the cells of plants. The term starch also covers a large variety of different substances of identical composition and similar properties. The variations of both are probably due to structural and molecular differences, but what these are is not known at present.

**Fermentation** is a general term applied to such reactions as are represented by the conversion of cellulose and starch to sugars and of the sugar into alcohol and of alcohol into carbon dioxide. As these processes take place in nature, they are usually, if not always, stimulated by the presence of a substance known as an enzyme, which in turn is usually, though not always, produced by unicellular organisms of the general type of bacteria. What the products of a fermentation process are depend in part on the enzyme present as a catalyzer and in part of course upon the substance fermented. There are three general types. (1) Total decomposition into very simple compounds is effected by molds and other similar organisms (putrefaction). (2) Decomposition involving the formation of acetic, lactic, and similar acids produced by definite varieties of bacterial organisms, which are essential to the formation of vinegar, and of sour milk, etc., by fermentation processes. (3) Decomposition involving fermentation of a simple sugar, which type of change is due to the enzyme of yeast and must be preceded by or accompanied by hydrolysis, if cellulose, starch or cane sugar is to be fermented.

Similar decompositions of albuminous material take place.

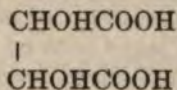
**Hydroxy Acids.** — If an organic compound contains an hydroxyl group and in addition a carboxyl group, we speak of it as an hydroxy acid. Two of these will be cited as illustrative of the group. Lactic acid,  $C_3H_5O_3$ , is in form a carbohydrate and a polymer of formaldehyde, but its synthetic preparation, which cannot be here detailed, shows it to have the structure  $CH_3CHOHCOOH$ . It is most readily prepared by the fermentation of the "wey" of milk, which contains a sugar known as lactose,  $C_{12}H_{22}O_{11}$ .

Lactic acid is of somewhat special interest because it contains one carbon atom which is combined with four different radicals. It has been found that when compounds contain such an atom,

called an asymmetric atom, at least three different modifications can be prepared which differ somewhat from each other, and in particular that one rotates the plane of polarized light to the left, one to the right, and the third is without effect on polarized light. Lactic acid is the simplest compound of this group.

It would lead too far to follow this topic further, but the reader's attention is called to the development from such considerations of a very comprehensive and satisfactory theory of the space relationships of the atoms of organic compounds which has been tremendously useful. The formulæ used to express such relations are known as stereo-formulæ. Stereo-formulæ were first suggested by Le Bel and van't Hoff (1871). Through Werner's hypothesis (*q.v.*) such space relations for many inorganic compounds find expression, and it may easily be that eventually we shall see with the "eye of the mind" the arrangement of all molecular structures in space. It is an interesting and inspiring extension of human vision.

The other hydroxy acid which is here discussed is tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ . It is given special mention for two reasons. It was through an investigation of its salts and those of its inactive modification, racemic acid, that the initial steps were taken by Pasteur (see Alembic Club Reprints, No. 14) which led eventually to the stereo-chemical view just mentioned. (For further details consult texts in Organic Chemistry.) It is also an important compound and its salts are extensively used. The structure of the acid is ordinarily expressed



It will be seen that it contains two asymmetric carbon atoms and Le Bel and van't Hoff's hypothesis calls for four compounds of this type. All four exist.  $\Delta$  Ordinary tartaric acid is found in many fruits, particularly in grapes, where it exists as the acid potassium salt,  $\text{KHC}_4\text{H}_4\text{O}_6$ , which crystallizes from wine and forms the most important component of the "lees" of wine. The crude deposit is known as tartar and by recrystallization the pure salt "cream of tartar" is prepared. The cream of tartar is the "acid factor" of many brands of baking powder (*q.v.*), of Seidlitz powders, and of "bromo seltzer," and finds other important uses. By neutralization of this acid salt the mixed salt,  $\text{NaKC}_4\text{H}_4\text{O}_6$ , is

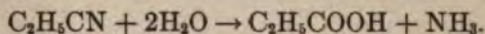


prepared. It is a common cathartic known under the name "Rochelle Salts." Tartar emetic,  $\text{KSbOC}_4\text{H}_4\text{O}_6$ , is also a familiar drug.  $\triangleright$

Mixed compounds of many other types and derived from other series are numerous and of practical and theoretical importance, but since our purpose is but to furnish a "Pisgah peep" at organic chemistry, it will be sufficient to call attention to their existence.

**Nitrogen Derivatives.** — There are several classes of nitrogen derivatives. The more important classes are those derived from cyanogen, from ammonia, and from nitric acid.

The cyanogen derivatives are known as nitriles and are prepared most readily by treatment of chlorides with potassium cyanide, *e.g.*,  $\text{CH}_3\text{Cl} + \text{KCN} \rightarrow \text{KCl} + \text{CH}_3\text{CN}$ . The nitriles of the paraffin series possess a special interest because they hydrolyze with water and produce acids which are derivatives of the member of the homologous series next larger than the radical from which they are prepared. Thus ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ , a derivative of ethane, with potassium cyanide, gives  $\text{C}_2\text{H}_5\text{CN}$ , which by digestion with water gives propionic acid, a derivative of propane:



The ammonia derivatives are formed by replacement of one or more of the hydrogen atoms of ammonia by organic radicals. The compounds which contain the  $\text{NH}_2$  group are especially important. They are known as amides or amines. To the group belong a very great variety of products of vegetable origin which are used for food. They are also abundantly represented in the animal body and the simpler compounds are the forms in which for the most part the worn-out nitrogenous material is excreted from the human body. (See urea.)

In the benzene series, the most interesting ammonia derivative is aniline,  $\text{C}_6\text{H}_5 \cdot \text{NH}_2$ , from which, more or less directly, the great body of aniline dyes are derived. The "bitter principles" of plants, the alkaloids, and the corresponding substances of animal origin, the ptomains, are also representatives of this type of compound.

The derivatives of the nitric acid type of most importance are those produced by replacement of the hydroxyl group of nitric acid by an organic radical. These are known as nitro-compounds and we have already mentioned picric acid, or trinitrophenol.

(See p. 288.) The nitro-compounds are especially characterized by the facility with which they decompose, furnishing gaseous products of oxidation with consequent large volume increase. They may therefore be used as explosives or as components of explosive mixtures.

The groups of derivatives containing nitrogen which have been mentioned are by no means all there are. For example, we have the pyridene group, the diazo compounds and the albumins. The last mentioned compounds contain sulfur, also, and the mention of gluten, egg albumen, nerve tissue, muscle, etc., will serve to indicate their importance.



## CHAPTER XXI

### SILICON AND BORON

**Occurrence.** — As has already been mentioned, silicon is, next to oxygen, the most abundant of the elements. Silicon compounds are more numerous than those of any other element save carbon. It does not occur in the free state in nature. In order to present a comprehensive view of the natural forms we may classify them and give a few examples of each class.

The oxide, silica,  $\text{SiO}_2$ , if crystallized is known as quartz, but this term covers a wide range of mineral forms. In separate crystals, it is known as rock crystal; if colored by traces of various impurities, it is known as amethyst, yellow, rose, smoky, or ferruginous quartz; if massive, *i.e.*, without distinct crystalline identity, as milky quartz. If not crystalline, it is known as chalcedony, agate, onyx, etc. If high in color due to impurities it is known as jasper. Nodules of amorphous silica are known as flint. Separate granules of silica, pure or impure, are the chief factors of sand. If sand grains are cemented together by amorphous silica, clay, etc., the substance is known as sandstone.

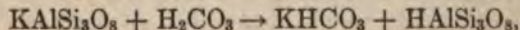
Hydrated silica,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , is known as opal, of which many mineral varieties are recognized, ranging from the jewel, which owes its value to variations in structure which give it high reflective and refractive power, to tripolite, which is a chalk-like material composed of the shells of diatoms.

The salts of orthosilicic acid,  $\text{Si}(\text{OH})_4$ , are also abundant in nature. Usually a silicate contains a given metal or metals as an essential constituent with more or less replacement by other similar metals. For example, garnet is an orthosilicate of magnesium and aluminium,  $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ , but the magnesium is frequently more or less completely replaced by calcium, iron or manganese, and the aluminium by ferric iron, chromium or titanium. It is usual to express the formula  $\text{R}_3''\text{R}_2'''(\text{SiO}_4)_3$ . Other orthosilicates are olivine,  $\text{Mg}(\text{Fe})_2\text{SiO}_4$ ; zircon,  $\text{ZrSiO}_4$ ; and epidote,  $\text{Ca}_2\text{Al}_2(\text{AlOH})(\text{SiO}_4)_3$ , etc.

The salts of metasilicic acid,  $\text{H}_2\text{SiO}_3$ , of greatest interest are: Leucite,  $\text{KAl}(\text{SiO}_3)_2$ , an important factor in lavas; pyroxene,  $\text{R}''\text{SiO}_3$ , where R is chiefly Ca, Mg, Mn, or Fe, an extremely common factor in igneous rocks; hornblende,  $\text{CaMg}_3(\text{SiO}_3)_4$ , of which asbestos is a variety. There are also many other minerals of this type.

**Polysilicates.** — Salts of silicic acids of complex type are found in nature and are grouped together as polysilicates (*vide* silicic acid). The more important minerals are orthoclase,  $\text{KAlSi}_3\text{O}_8$ , and albite,  $\text{NaAlSi}_3\text{O}_8$ . These are important because of their relation to rock and soil formation (*vide infra*). All the silicates so far mentioned are to be considered as neutral salts and are anhydrous. There are also silicates in great variety, which on ignition give water; these are either acid salts or contain water of crystallization. These are usually divided into four groups, the zeolites; the micas, of which muscovite,  $\text{H}_2(\text{K} \cdot \text{Na})\text{Al}_2(\text{SiO}_4)_3$ , and biotite  $\text{H}_2(\text{Mg} \cdot \text{Fe})\text{Al}_2(\text{SiO}_4)_3$ , are examples; the serpentines, of which serpentine,  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ , and talc,  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ , are examples; and the kaolins, of which kaolin,  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ , and ordinary clay are examples. There are also "subsilicates" or basic salts, of which tourmaline is an example. Besides all these varieties of *minerals silicate rocks* form the bulk of the crust of the earth. These are aggregates of minerals and examples are granite, syenite, gneiss, basalt, etc.

**Soil Formation.** — When rocks or the minerals of which they are made up are subject for long periods of time to the action of carbon dioxide, moisture, oxygen and alternate heating and cooling, the effect is more or less complete disintegration and the insoluble residue is known as "soil." From the nature of the rocks it follows that two factors predominate in soils. These are clay and sand. As commonly used, both terms cover a wide variety of different materials, but since orthoclase may be taken as a typical silicate and by weathering produces an acid silicate,



the latter compound may be considered as a typical clay. As the different rock components are unequally affected by weathering, the soils will contain varying amounts of undecomposed minerals. The original products of weathered rocks are moved from place to place by water transport and by winds. As plants grow on soil



and partially decay the soils become more and more intermixed with organic substances. Finally all soils, at least all fertile soils, are the habitat of a great variety of bacterial forms of life. It follows, then, that a given sample of soil may be, and usually is, a very complex mixture of substances.

**Uses.** — Silica and the silicates as they occur in nature are utilized to a very great extent and the industry which concerns itself with their preparation for market is of great importance. The most valuable materials are those used for building stone; granite, sandstone and slate. Many of the siliceous materials are prepared for industrial purposes by various manufacturing operations.

Talc is cut or ground for use as a filler in paper manufacture, as a lubricant, in the preparation of cosmetics and certain soaps, for gas tips, for slate pencils, for electrical switchboards, baths, sinks, crucibles, furnaces, table tops, etc. The micas are prepared for use in electrical devices, for stove and furnace doors, for covering for steam boilers, for spangling wall paper, in calico printing, for ornamentation of porcelain, etc.

Asbestos, which is serpentine or hornblende in fibrous form, is used to make non-inflammable paper, cloth, boiler and steam pipe covering, yarn and rope for packing valves, etc. Feldspars are used in large quantity as glazing material for pottery (*q.v.*).

Quartz in various forms is used in great quantities as decorative building material, for the manufacture of glass, porcelain, plaster, concrete, sandpaper, whetstones, grindstones, as an abrasive in soaps and scouring powders, etc. Over a million tons of sand a year are produced in this country alone. Tripoli, or infusorial earth, is used in filters, polishing powders, dynamite and in various other ways.

Kaolin and other varieties of clay are used in the manufacture of brick, cement, earthenware, pottery, porcelain, sewer pipes, etc. A specially fine grained clay, known as fuller's earth, is used as a filtering material for clarifying and bleaching mineral oils, lard and cottonseed oil. Finally, certain varieties of siliceous minerals are used as gems. Examples are beryl, opal, garnet, topaz, chrysolite, tourmaline, etc.

**History.** — The use of siliceous materials by man dates back to prehistoric times and even the manufacture of glass is of uncertain antiquity. The recognition of the fundamental character

of silicon dioxide as an acidic material we owe to Scheele, 1773, Berzelius in 1823 prepared amorphous silicon. Crystalline silicon was first made by St. Clair Deville in 1854.

**Preparation.** — If an active metal, such as sodium or potassium, is heated with silicon fluoride or silicon chloride an amorphous powder is produced. The same material may also be prepared by passing the vapor of silicon tetrachloride over molten aluminium. The aluminium chloride formed volatilizes and the silicon dissolves in the excess metal from which it crystallizes in long lustrous crystals. Huge quantities of silicon are prepared by the simultaneous action of carbon and iron on silica incident to the preparation of pig iron, which contains about 2% silicon (see pig iron manufacture).

**Properties, Physical and Chemical.** — The element in its amorphous form is a brown powder. It does not react with acids. It unites fairly readily with chlorine, bromine and oxygen when heated. It also combines readily with nitrogen at high temperatures. It will decompose hydrochloric acid gas at high temperature and is slowly dissolved by aqua regia and the corresponding mixture of hydrofluoric acid and nitric acid. It has a specific gravity of 2.85 and melts at about  $1500^{\circ}$ . The crystalline variety is harder than glass and varies in specific gravity according to mode of preparation from 2.35 to 3.0. It is less active chemically in general than the amorphous variety.

The element is not prepared in large quantity, except incidentally as a by-product, since it does not as yet find extensive use. The crystals are used as coherers in wireless telegraphy.

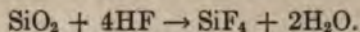
#### COMPOUNDS

**Silicon Hydrides.** — Silicon forms with hydrogen a series of compounds analogous to those of carbon, but much fewer in number. Only three are certainly known. These are silico-methane,  $\text{SiH}_4$ , silico-ethane,  $\text{Si}_2\text{H}_6$ , and silico-acetylene,  $\text{Si}_2\text{H}_2$ . It is conceivable that others and their derivatives may be prepared. These "hydrosilicons" may be most readily prepared by treatment of metallic silicides with acids, e.g., magnesium silicide,  $\text{Mg}_2\text{Si}$ , when treated with concentrated hydrochloric acid, gives a spontaneously inflammable mixture of hydrogen, "silicane,"  $\text{SiH}_4$ , and silico-ethane,  $\text{Si}_2\text{H}_6$ . This may be illustrated, using the same type of apparatus as

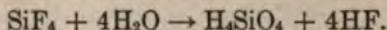


was used for arsine and phosphine (Fig. 80). Pure silicane is not spontaneously inflammable, but burns readily to silica and water (*cf.* p. 302).

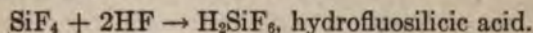
**The Halides.**—Of the halides the most interesting is silicon tetrafluoride,  $\text{SiF}_4$ . It was discovered by Scheele. It is made by direct treatment of silica or of silicates with hydrofluoric acid.



It is a colorless, insoluble gas with a characteristic odor. If it is passed into water some of it is hydrolyzed:



The hydrofluoric acid so produced unites with the fluoride to form a soluble acid:



This acid or its salts finds use in artificial petrification of wood, as an electrolyte in the electrolytic manufacture of lead and in other ways of less moment. The chief interest of the silicofluoride lies in its incidental preparation in the process of etching glass (*cf.* p. 148).

From the halides of silicon, particularly silicon tetrachloride, a considerable variety of derivatives have been made, such as:  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{SiHCl}_3$ ,  $\text{SiH}_2\text{Cl}_2$ ,  $\text{Si}(\text{NH}_2)_4$ , etc., for details of which the reader is referred to larger works.

**Silica and the Acids of Silicon.**—Silicon dioxide like carbon dioxide is the anhydride of an unstable acid. When silicon tetrachloride is hydrolyzed the products should be, by double decomposition,  $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{HCl} + \text{Si}(\text{OH})_4$ , hydrochloric acid and orthosilicic acid. If the attempt is made to isolate this substance by evaporation, a jelly-like substance is obtained. It is appreciably soluble in water. When the solution is dialyzed, a solution is obtained which contains about 5% of silica. The process of dialysis is carried out interposing between the solution and pure water a parchment or similar membrane, through which the hydrochloric acid or soluble salts may pass (Fig. 88). The silicic acid appears to be in *colloidal solution*, *i.e.*, while so finely divided that it will pass through filter paper and remain indefinitely in suspension, it does not modify the freezing and boiling points of water and otherwise behaves differently from true solutions.

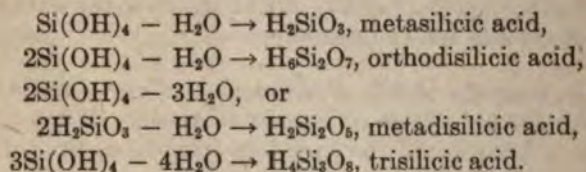
Many other substances are capable of existing in colloidal condition. Examples are finely divided metals, aluminium hydroxide, ferric hydroxide, starch, etc. Colloids of this sort are known as *hydrosols*. If acid is added to a solution of a soluble silicate or if a strong solution of the hydrosol is allowed to stand, a jelly-like mass forms, known as a *hydrogel*. This jelly, if air dried, contains about 16% water, but if heated, the water content decreases until at about 500° anhydrous silica remains. The hydrogel if dried *in vacuo* over sulphuric acid has approximately the composition corresponding to the formula  $\text{H}_2\text{SiO}_3$ , or metasilicic acid. This form is readily soluble in sodium carbonate or hydroxide and indeed reacts appreciably with hydrochloric acid. The higher the temperature to which the silicic acid is heated the



FIG. 88.

less soluble it becomes until if heated to 1000° it is practically insoluble. This behavior of silicon dioxide is also shown by certain other oxides and notably by aluminium oxide (*q.v.*).

It is doubtful if definite hydrates of silica are formed. It is nevertheless the case that definite minerals are found and certain compounds are prepared artificially which indicate the relationship shown by the following formulæ:



The occurrence of salts of these acids has already been discussed (*vide p. 365 et seq.*).

Silica can be melted at about 1600°, and when cooled it forms a vitreous mass known as *quartz glass*. The coefficient of expansion of this glass is very small, and in consequence the material may be heated or cooled quickly without fracture.

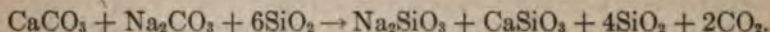
**Glass.** — Molten silica forms homogeneous mixtures with silicates, *i.e.*, solutions, which when cooled do not separate nor crystallize. In the process of cooling the liquid mass shows no definite



transition point from the liquid to the solid state. These solutions are known collectively as *glass*, and at the ordinary temperature may be regarded as very viscid liquids.

Glass is ordinarily made by fusion of quartz, or pure sand, with sodium carbonate and limestone in proper proportions to make the fused residue have the composition  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ . For cheap varieties of glass sodium sulfate and charcoal may be used instead of soda. Since perfectly pure materials are expensive, more or less impure substances are used, and the consequent colors are compensated by addition of suitable quantities of manganese dioxide or of selenium. The various kinds of glass are of three types according to the method of treatment of the fused material, *viz.*, "blown," "blown in the mold," and "cast."

To make glass the raw materials are mixed in the proper proportions and heated to a temperature just below the melting point to permit the reaction to take place. This may be expressed:



The gases are allowed to escape and the temperature raised to the melting point, about  $1200^\circ$ , and kept hot until a quiet fusion is obtained. The crucible is then allowed to cool to about  $800^\circ$ , when the glass is pasty. Suitable masses are then collected on long metal tubes and blown by the workmen into the desired form. For window glass, long cylindrical bottles are blown, and when cold the ends are cut off by wrapping a string of hot glass around the cylinders and touching the heated ring with a cold iron point. A crack instantly follows the string of glass around the portion heated. The cylinder so produced is split lengthwise by means of "marking" it with hot iron and touching the hot streak at one end with cold iron. The split cylinder is then placed in a furnace and heated until it flattens out to a smooth sheet. It is then annealed by being cooled very gradually, and when cool is cut into desired sizes. If annealing is not well and carefully done, the glass is brittle and readily cracked. Beakers, flasks, test-tubes and all better grades of glassware are blown by hand. Glass tubing is made by making first a hollow globe of glass and rapidly drawing it out to the desired diameter. Bottles and other cheap glass articles are usually blown into suitable molds. Cast glass is made by running molten glass into flat pans of suitable dimensions, and when cold the sides are ground until smooth and then polished. The most important variety is "plate glass." The art of blowing

glass is one which requires a long apprenticeship and a high degree of skill.

Glass is also graded according to composition. Common glass has the composition previously indicated, but it softens readily when heated, and is rather readily soluble. For chemical purposes a less fusible and less soluble glass is made by substituting potassium carbonate for sodium carbonate. This is known as Bohemian or hard glass. Lead carbonate and potassium carbonate may be used with silica to produce a glass with a high index of refraction suitable for use in optical instruments. It is heavy and soft, and by grinding, "designs" may be cut into its surface. This is known as cut glass. Cavalier glass, jena glass and many other special varieties of chemical glassware are made by using potassium carbonate or zinc carbonate, and, in lieu of a portion of the silica, boric acid.

Molten glass will dissolve many oxides of metals, since it apparently contains silica capable of reacting thus:  $\text{Cu}_2\text{O} + \text{SiO}_2 \rightarrow \text{Cu}_2\text{SiO}_3$  (cf. phosphates, p. 305, and borates, p. 380), and many of these oxides produce colored glasses. Thus cobalt oxide gives blue, chromium green, uranium yellow, cuprous oxide ruby, etc. Colloidal suspensions of finely divided materials also produce special glasses, e.g., gold produces a deep red color, stannic oxide milk glass, etc. It was in the study of these glasses that the ultramicroscope was developed.

**Pottery, etc.** — Clay becomes plastic when moist and can be molded into desired forms. When dried, it shrinks and becomes hard, but is fragile. It may be made stronger by using fibrous material in the molded mixture. Air-dried materials of this type were manufactured many centuries ago and used in building operations and for many other purposes (cf. Exodus 5:7). When heated to a high temperature the molded clay retains its shape and acquires considerable mechanical strength. It loses the power of again becoming plastic with water (cf. p. 371). These properties have given clay working a most important place in industry. From it are made various types of material which may be classified into three groups: Porcelain, pottery and brick.

*Porcelain* is the name applied to the highest grade of ware made from clay. It is made by grinding very pure kaolin with feldspar and making up to a plastic mass by addition of water. It is then molded into the desired forms, dried and fired at a



temperature of about  $1200^{\circ}$ . This forms the so-called "biscuit body," which is then glazed by dipping in a thin paste of feldspar, or a mixture of suitable type, and refiring. The glaze melts and forms a homogeneous translucent cover for the clay body. Such ware is used for tableware under the name "china." If less pure clay is used and less care is used in glazing we have various grades of *pottery*. Unglazed pottery is used for tile, flower pots, etc.

If the clay is burned alone, the product is known as *brick*, and, if heated to incipient fusion in burning, as "vitrified brick." Fire brick have an excess of free silica. The color of brick depends upon the quantity and character of the impurities of the clay. The red color is due to ferric oxide.

### BORON

**Occurrence.** — Boron, though in a different periodic group and with a different valence, has many properties relating it to silicon. In other respects it is similar to the metals (*vide infra*). It forms, therefore, a very striking "border line" element (see periodic table).

It is found in nature ordinarily either as free boric acid, as in the fumeroles of Tuscany, or as some more or less modified salt of the same acid (*vide infra*). These forms are **tincal**, crude borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , found in Thibet and India and especially in southern California; **colemanite**,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ; **ulexite**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot (\text{CaB}_4\text{O}_7)_2 \cdot 18\text{H}_2\text{O}$  and **borocite** ( $\text{Mg}_3\text{B}_3\text{O}_6$ ) $\text{MgCl}_2$ , etc.

**History.** — The term **borax** is of ancient and uncertain origin, but the name **boric acid** came to be used for the free acid following Lavoisier's revision of terms. Impure boron was first made in 1808 by Gay-Lussac and Thenard, and practically pure boron by Moissan in 1892. Recently Weintraub (Jour. Ind. and Eng. Chem., Vol. 5, p 106) has prepared boron by first reducing the trioxide with magnesium and then fusing the element in an electric furnace.

**Preparation and Properties.** — The element may be prepared in both the amorphous and crystalline form. The amorphous form is rather readily attacked by oxidizing acids and is at high temperature capable of reducing both silica and carbon monoxide. In both the amorphous form, as prepared by Weintraub, and

the crystalline form, as prepared by solution of boron in molten aluminium, and from which it crystallizes on cooling, boron is very hard, yielding only to the diamond. It is brittle and when cold is a very poor conductor, but at 400° C. its conductivity has increased over two million fold. In this respect it is similar to, but more remarkable than, carbon. The element unites very readily at high temperature with nitrogen to form the nitride.

In general, boron behaves as a non-metallic element in that its hydroxide behaves as an acid, though a very weak one, and its halides hydrolyze with water. It also forms a double fluoride,  $\text{HBF}_4$ , hydrofluoboric acid, analogous to hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ . On the other hand, boric oxide reacts with concentrated sulfuric and phosphoric acids to form readily hydrolyzed salts,  $\text{B}(\text{HSO}_4)_3$  and  $\text{BPO}_4$ .

The element has as yet no very extended uses, though its remarkable change of conductivity with temperature points to probable future application. The only compounds which need detailed discussion in this place are boric acid,  $\text{B}(\text{OH})_3$ , and its derivatives.

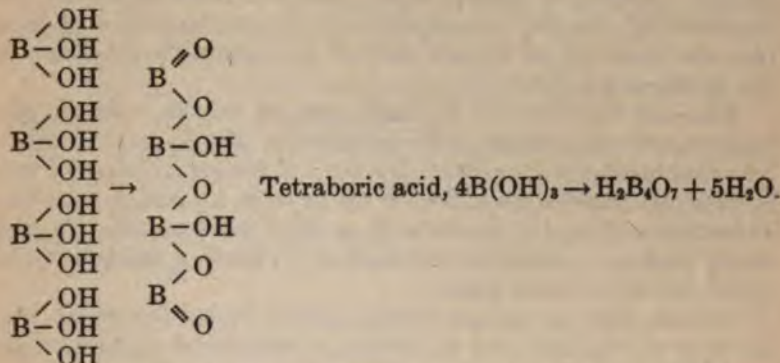
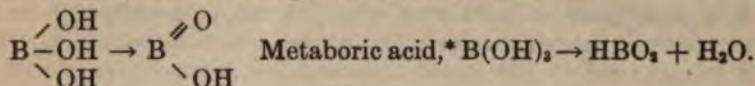
**Boric Acid.** — Boron trichloride can be made by direct union of boron and chlorine, or by heating boric oxide and carbon in a stream of chlorine or by treatment of boron or boric oxide with hydrochloric acid. If the trichloride is treated with water a reaction takes place which can scarcely be other than  $\text{BCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{B}(\text{OH})_3 + 3\text{HCl}$ . The trihydroxide should behave itself as a tribasic acid and undoubtedly does so though but few orthoborates have been prepared. That it does so act is shown by the existence of magnesium orthoborate, and more particularly by the formation of triethyl borate  $\text{BO}_3(\text{C}_2\text{H}_5)_3$ , a volatile compound the vapor density of which corresponds with the formula given. This compound is formed when borax and alcohol are heated with sulfuric acid. It burns with a green flame. This is the ordinary qualitative means of detecting boron (see Fig. 89). Boric acid salts are, however, usually not ortho-salts, which may be due to the fact that the second and third stages of ionization,  $\text{H}_3\text{BO}_3 \rightarrow \text{H}^+ + \text{H}_2\text{B}'\text{O}_3 \rightarrow \text{H}^+ + \text{HB}''\text{O}_3 \rightarrow \text{H}^+ + \text{BO}_3'''$ , do not readily take place with a weak acid (*cf.* p. 306), as is to be expected from the law of mass action. It is more probably due



FIG. 89.



to the facility with which the ortho-acid loses water to form the meta-acid and "condensed" acids analogous to those of silicic acid (*q.v.*). The relationships of the two more important of these are shown by the following constitutional formulæ:

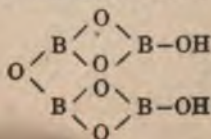


The salts of both the meta- and tetra-acids are found in nature (*vide* occurrence).

By complete dehydration of the trioxide the anhydride is formed,  $2\text{B(OH)}_3 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$ .

**Borax.** — The above relations have special interest because of the extensive uses of **borax** (sodium tetraborate.) It may be made by digesting boric acid, which is but slightly soluble in water, with soda ash and evaporating the solution to crystallization when the crystals,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , are formed. It is usually made by recrystallization of the crude borax found in nature or by digesting

\* The molecular formula of metaboric acid is not known and it may be  $\text{H}_3\text{B}_3\text{O}_6$ , and hence have the structure  $\text{HO}-\text{B} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{B}-\text{OH}$ , and by elimination of water from two molecules of this the tetraboric acid may have the formula:

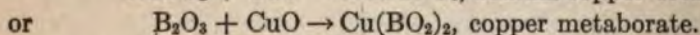
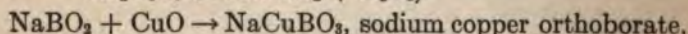
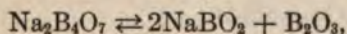


the calcium ores with soda ash and crystallizing the solution formed. The borax so prepared is used in the manufacture of glass and enamels; as a preservative, since like the acid it has antiseptic power; as a toilet preparation (borated talcum powders); as a flux in welding and assaying, and for the preparation of boric acid which is used extensively for various medical purposes. Borax is also used in the manufacture of toilet soaps; as a mildly alkaline material in laundry work; and in a large variety of other applications. In the laboratory it is frequently employed to detect the presence of certain metals by means of the bead test (*cf.* p. 305 and p. 376).

The salt functions in the same general way in welding, glass-making, and assaying as in the bead test. The hydrate is efflorescent and hence loses water in dry air. If heated, the loss of water is hastened and the borax swells up to form a white porous mass. If heated sufficiently it melts to a clear vitreous mass, a glass, which does not crystallize on cooling. This is a market product under the name **borax glass**.

If this glass is melted with metallic oxides the fused borax dissolves the oxides, and in certain cases colored glasses are produced which are frequently characteristic.

We may regard the anhydrous borax as a solid solution of sodium metaborate and boric anhydride and formulate the reactions as:



Which reaction really takes place is immaterial since as carried out in bead or glass making, there is a large excess of the unaltered borax. Of course with the oxides of trivalent elements the reactions are analogous. In welding, the borax dissolves adhering oxides and being liquid at the welding temperature is squeezed out, leaving clean surfaces for welding contact.

**Exercises.** — 1. A mineral is found which on analysis shows as follows:

	Per cent.
Silica, $\text{SiO}_2$ .....	66.21
Alumina, $\text{Al}_2\text{O}_3$ .....	19.16
Potassium oxide, $\text{K}_2\text{O}$ .....	7.38
Sodium oxide, $\text{Na}_2\text{O}$ .....	7.25



What is the empirical formula when written  $K_x(Na)Al_ySi_zO_w$ ?

2. Write all the reactions involved when silica and calcium fluoride are treated with concentrated sulfuric acid and the products are passed into water.

3. How many grams of sodium carbonate must be used to convert 10 grams of pure quartz to sodium metasilicate? Why is it desirable to use an excess?

4. If sodium silicate in aqueous solution is treated with ammonium hydroxide silicic acid is formed. Write the equation for the reaction and explain.

5. When boron nitride reacts with steam, boric acid and ammonia are formed. Write the equation.

6. Write equations showing the preparation of triethylborate  $(C_2H_5)_3BO_2$  when borax, alcohol, and sulfuric acid are mixed.

7. Compare the behavior of boric anhydride, silica, and phosphoric anhydride by writing equations for the formation of meta-salts by heating with cupric oxide. Also with chromic oxide,  $Cr_2O_3$ .

8. Write the structural formula for trisilicic acid showing its derivation from orthosilicic acid.

9. Make a list of the elements so far discussed which show evidence of existing in allotropic forms.

## CHAPTER XXII

### THE METALS

**General Characteristics.**—The origin of the term "metal" is uncertain. It seems to have arisen from the Greek, μέταλλον (to explore), and to have reference to the fact that metals were secured by search. The meaning which attaches to the word varies greatly with the connection in which it is used. In printing the word is used to describe the alloys used. In road building the word is used to describe the material used as ballast. In glass factories the fused materials are spoken of as metals. In chemistry the use of the term has varied greatly as the viewpoint of the students of the subject has changed. At present it is used as a general term to describe a group of **elements**. For convenience in discussion it has long been customary to divide the elements into two groups, the **metals** and the **non-metals**. This division is purely mental and sharp lines of demarcation cannot be drawn. This inherent difficulty of classification is so marked in the present case that we sometimes attempt more definite separation of the groups by creating an intermediate one, the **metalloids**, which possess properties common to both groups. It is doubtful if any great advantage is so gained. In general we regard as non-metals those elements which form acidic oxides, do not react with mineral acids to liberate hydrogen, and form volatile acids with hydrogen. We also expect their halogen compounds to hydrolyze readily. From the standpoint of physical properties we expect them to be gaseous, or readily volatile, not usually opaque, to have low specific gravities, to be bad conductors of heat and electricity, and to be neither malleable nor ductile. By contrast with these, which include the elements so far discussed, we find many elements which form basic oxides, which react with mineral acids to form salts with evolution of hydrogen, which either do not unite with hydrogen at all or with it form unstable compounds. The halogen compounds of these elements are not readily or extensively hydrolyzed. In physical properties we likewise encounter contrast. In general



the metals are solid, opaque, have high specific gravities, are good conductors of heat and electricity and are both malleable and ductile.

It is obvious to any one with even a slight acquaintance with the elements that few, if any, of them possess all the characteristics of either group. Thus carbon and silicon are non-volatile and the hydrogen compounds are not acid. Similarly the metal mercury is liquid and caesium and several others are readily liquefied. Lithium, sodium, potassium and aluminium are not of high specific gravity. In spite of these difficulties the distinction between the two types is useful though we do not expect nature to adapt itself to our specifications.

Of the sixty to sixty-five elements usually grouped under the head "metals" about ten are classed as "common" because they or their compounds are of widespread occurrence in nature, and about fifteen more are regarded as common, because they find extensive direct or indirect application in the arts. By contrast with these the remainder are known as **rare elements**. Here again we encounter great difficulty in establishing an artificial boundary. Changing times and new discoveries of applications sometimes make a previously rare substance familiar. Thus cerium and tungsten, usually classed as rare elements are by their use in the Welsbach burner (*q.v.*) and the electric light (*vide tungsten*) used in literally millions of homes, while the more common titanium is little more than a curiosity. We usually list as common metals the following: Iron, aluminium, copper, lead, tin, mercury, zinc, calcium, magnesium, sodium, potassium, barium, strontium, chromium, manganese, cobalt, nickel, cadmium, bismuth, and silver. We include also the "metalloids," arsenic and antimony, but exclude the fairly common titanium and lithium. In subsequent discussions we shall to some degree indicate the relative importance of the elements by fullness of description.

**Occurrence.**—Very few of the metals occur free in nature. When they do they are said to be "native." Native metals are usually more or less finely divided and distributed through a matrix of rock or in alluvial formations produced by decomposition of rocks. The metals which so occur are copper, mercury, gold, silver, platinum, and rarely, iron.

When compounds of metals suitable, or presumably suitable, for commercial preparation of the metals are found in nature they are

termed "ores." (The term is sometimes extended to hard matrices containing the native metals.) When natural compounds of the metals not used as ores occur they are spoken of as "mineral forms."

The subsequent discussion will take up the ores and chief mineral forms of each metal and it is only necessary here to call attention to the fact that the chief ores are the oxides, hydroxides, sulfides and carbonates of the metals. The most abundant mineral forms are the silicates.

**Preparation.** — The various modes of winning the metals, not only from their ores, but the isolation of them from mixtures, and the conversion of the metal into useful forms is known as "metallurgy" and is so large a subject that it is usually made a separate topic of study. In subsequent pages the methods employed for the preparation of individual metals will be given in some detail. It is the purpose here to give the general character of the problem and the types of methods used. In general the method employed varies so much with the character of the metal sought and the ore used that for each ore the problem is individual. Usually, also, the metal is not only to be separated from its compound but also from admixed material known as "gangue." It is also usually necessary in order to obtain the metal in large quantities and in a state approaching purity, to prepare it at a temperature above the melting point, so that it may be removed from the furnace in liquid form. To secure these ends the ore, with its gangue, is mixed with a "flux," which will form with the gangue a liquid "slag" and with a fuel, which by combustion, not only may assist in reaching the required temperature, but also "reduces" the metal. The chief methods may be catalogued as follows:

1. **Reduction by Carbon.** Many of the ores are oxides. In most cases the oxides are reduced when heated with carbon, either in the form of charcoal or coke. The carbon being converted according to circumstances into the monoxide or dioxide escapes and, if with the charge suitable fluxes are used and a sufficiently high temperature employed, both the metal and impurities are removed in liquid form. This method is known as "smelting" and is employed on a vast scale in the preparation of metals, particularly iron and copper.

In many cases ores, not oxides, may, by heating in the air, be converted into oxides. The process is usually called "roasting," and the roasted ore is then smelted with carbon.



**2. Reduction by Metals.** In many cases oxides cannot be profitably reduced by means of carbon and in some not at all. In still other cases the metal unites, after reduction, with carbon and hence a pure product cannot be obtained. In such cases it is possible to use a cheaper metal to reduce the oxide of a more expensive one. The metal usually so employed is aluminium and the process is called the **Goldschmidt method**, from its inventor (Fig. 90). Other metals may also be employed. The following equations will illustrate the process:

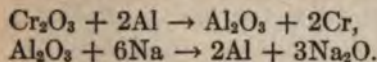
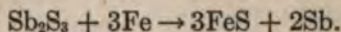


FIG. 90.

**3. Reduction of Sulfides by a Metal.** Just as oxygen may be removed by aluminium from an oxide, so sulfur may be removed from a sulfide by fusion with a metal, *e.g.*,



**4. Reduction Using Electric Heat.** In the preceding methods the reducing agent employed not only effects the reduction but also its combustion furnishes the needed temperature. If, however, an electrically heated furnace is employed, not only may the desired temperature be readily reached, but the amount of reducing agent used may be more accurately regulated. This is frequently so desirable that electrically heated furnaces are being used in metallurgy with increasing frequency.

**5. Electrolytic Reduction.** When ores can be brought into solution it is possible, provided the solutions are electrolytes, to decompose them by electrolysis and this method is of rapidly-growing importance. Only in a comparatively few cases can aqueous solutions be employed, but it is possible to obtain electrolytes by melting either the ore itself, or the ore with a suitable flux, which may be then electrolyzed. (*Vide* aluminium.) This method, the deposition of metals by electrolysis, is employed not only to

prepare metals from their ores, but also to purify the crude metal obtained by one of the above methods. (*Vide* copper.)

**6. Displacement Methods.** In certain cases it is desirable to prepare soluble salts of metals and then precipitate the metal by using another less costly metal which is higher in the electromotive series. This method is employed especially in the metallurgy of silver and gold (*q.v.*)

**Physical Properties.**—Certain of the properties of the metals have been indicated in the preceding paragraphs. When the attempt is made to catalogue the properties of the metals the difficulty is encountered that in many cases these vary somewhat according to the method of manufacture or subsequent treatment. When numerical values are given they should not be understood as rigidly correct. In general, metals have, when in compact masses, a **luster** which is hence called metallic. Usually when powdered, this luster disappears, and the metals are all black and lusterless. Powdered magnesium and aluminium are exceptions. Usually also metals are **silver white**, but copper and gold are exceptions. Metals can all be obtained in **crystalline form**, but are usually encountered in massive form, because in cooling the process is rapidly carried on and the crystallization is not distinct. Tin and zinc, however, are often distinctly crystalline. The crystalline form is ordinarily cubical.

The **specific gravity** of metals ranges from that of lithium, 0.53, to osmium, 22.5. A table of specific gravities of the elements is found in the appendix. Very frequently the term "heavy metals" is used to include those with a specific gravity greater than five, and "light metals," those of a lesser specific weight. The heavy metals are in general less chemically active than those of low specific gravity. In general, metals are malleable, but those which are sometimes called metalloids are brittle. The malleability is very greatly modified by small amounts of impurities and also by the temperature. Most metals are brittle at sufficiently low temperature. Copper offers a remarkable exception, being still flexible, and presumably malleable, at the temperature of liquid air.

The relative tenacity, or **tensile strength**, of metals is not the same as their relative malleability and varies not only with the different metals but with the heat treatment of each, and also with the presence of small quantities of impurities. It is measured in



terms of the number of pounds per square inch, or kilograms per square millimeter, a piece of the metal can sustain without breaking.

The **hardness** of metals is measured by comparison with an arbitrary scale and refers to the relative ease with which they may be cut by a sharp instrument. The metals vary in hardness from caesium, which is softer than talc, to chromium, which is nearly as hard as corundum. The hardness of metals is very materially influenced by small quantities of foreign materials.

The **melting point** of metals is a very important property and varies from  $-38.7^{\circ}$  for mercury, to about  $3000^{\circ}$  for tungsten. A table of melting points appears in the appendix. The influence of dissolved substances on the melting point of metals is very marked, so that small amounts of impurities alter the melting points of metals enormously.

The **boiling point** of metals is relatively high, *i.e.*, the range of temperature within which they are liquid is large. Thus, mercury melts at  $-38.7^{\circ}$  and boils at  $357^{\circ}$ , while sodium melts at  $97^{\circ}$  and boils at  $877^{\circ}$ . Yet in several cases the volatility of metals is utilized in their metallurgy, notably in the cases of zinc and cadmium.

The **conductivity** of metals for heat and electricity distinguishes them fairly sharply from non-metals, since in general non-metals are very poor conductors. The metals vary in this respect widely among themselves and also vary with the temperature. In contrast with the non-metals, however, their electrical conductivity increases with lowered temperature (*cf.* boron). The unit of electrical conductivity is the reciprocal ohm or mho, which is the conductivity of a column of mercury at  $0^{\circ}$ , 106.3 cm. in length and 1 sq. mm. cross section. A table of relative conductivities appears in the appendix.

When metals are in the liquid state, *i.e.*, molten, they act as solvents for many non-volatile substances and in most instances for gases also. The solution of gases has been discussed (*vide* occlusion). When non-volatile substances dissolve in liquid metals, compounds are formed in some instances, *e.g.*, carbides, and in other instances the properties of the resulting substances are more readily classified as solutions. When the dissolved material is another metal, the solution is called an **alloy**. A table of the composition and names of the commoner alloys is also found in the appendix. The same general relation obtains between liquid metals as between other liquids, *i.e.*, some are

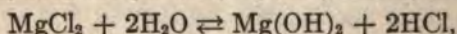
miscible in all proportions. Some are miscible within limits and others are practically immiscible. One type of alloy is especially readily formed by the lighter metals, that with mercury, and these alloys, as well as those of mercury, with the heavy metals, are known as amalgams. The discussion of the question as to whether alloys are chemical combinations or not is as futile as is the same question with regard to other solutions. Undoubtedly in certain cases definite chemical combinations are produced.

**Chemical Properties.** — It is difficult to classify the chemical properties of the metals in such a way that the statements will apply to all. In general, we may say that the following may be considered as typical of the class.

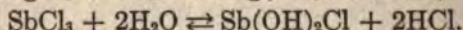
1. **Ionic Relations.** The compounds of the metals, if soluble, are ionized to some degree and the cation is usually the metallic factor.

2. **Basic Oxides.** The oxides may be either soluble in water or insoluble, but if soluble the solutions are bases, and consequently may react with acids to form salts. The insoluble oxides likewise react with acids to form salts in which the metal forms the positive ion.

3. **Halide Compounds.** The halogen compounds of the metals are not notably hydrolyzed by water, but are ionized. This property is utilized to distinguish metals from non-metals. It is to be noted that continuity is to be observed here, as elsewhere, and the more nearly the elements approach acid character the more markedly are they hydrolyzed. In some instances elements typically metallic in physical properties are almost typically acid in this respect. Thus, magnesium chloride, ferric chloride, aluminium chloride, etc., are partially hydrolyzed, *e.g.*,



and



Even in these latter cases the reactions are readily reversible, which is not the case with non-metals.

4. **Acidic Oxides.** The oxides and hydroxides of metals are as a rule basic, but certain of them are markedly amphoteric in character (*cf.* pp. 183 and 477). It is also true that where the elements have varying valence the oxides and hydroxides of higher valency are more acidic in character. This variation is

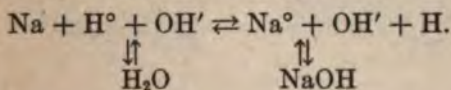


specially marked with manganese, where the simplest oxide,  $\text{MnO}$ , is strictly basic, while the heptoxide,  $\text{Mn}_2\text{O}_7$ , is the anhydride of the strongest of all the acids.

**5. Double and Complex Salts.** Certain metals form salts capable of combination with certain other salts to form **double** or **complex** salts. These salts apparently ionize in such a way that one of the metals forms part of complex negative ions. Examples are the double halides (*q.v.*), the complex cyanides (*q.v.*), the alums, etc. These salts are sometimes divided into two groups: the more stable, such as  $\text{K}_3\text{Fe}(\text{CN})_6$ , showing little or no reversibility in aqueous solution, and known as complex salts, and those in which solution appears to effect nearly complete dissociation, known as double salts, an example of the latter being ordinary alum (*q.v.*).

**6. Complex Cathions.** Certain metals form parts of complex cathions. An example of this is furnished by silver salts with ammonia, where the positive ion is  $\text{Ag}(\text{NH}_3)_2^+$ .

**7. The Electromotive Series.** When a metal is placed in water an electrical charge is developed upon that portion which does not go into solution. According to Nernst this is due to a tendency of the metal to go into solution as an ion. For example  $\text{Zn} \rightleftharpoons \text{Zn}^{++}$ . In some cases this tendency is so strong that hydrogen ions from water are discharged and the process of solution continues to exhaustion of either metal or water, *e.g.*,



In other cases the reaction reaches equilibrium before any hydrogen is evolved, for example, a stick of zinc in water. In such a case a negative charge is developed on the zinc stick. The intensity of the charge may be

measured by making an electric couple out of the zinc stick and an electrode of known potential. See Fig. 91. In case the metal is placed in a solution of its own salt it is evident from the law of chemical equilibrium that the presence of the metal ions already in solution would lessen the tendency of the metal to ionize and in certain cases this **precipitation** tendency may be in excess of the

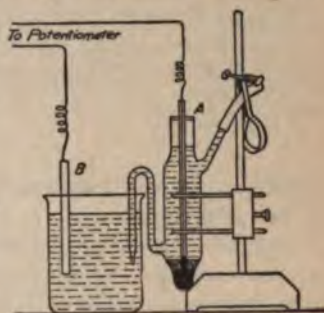


FIG. 91.

solution tendency, and ions may deposit upon the metal, in which case the metal would be positively charged.

If now the metals are compared with respect to the character and intensity of electrical charge assumed by them when in contact with a solution normal with respect to their ions they are found to arrange themselves in the order given (see table of the Electromotive Series), and this series is known as the electromotive series (and is extended to include also the non-metals).

**Electrochemical Series (Electromotive Series)**

*Metals —*

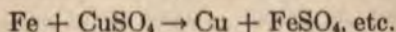
Caesium	Manganese	Arsenic
Rubidium	Zinc	Copper
Potassium	Cadmium	Mercury
Sodium	Iron	Silver
Lithium	Cobalt	Palladium
Barium	Nickel	Platinum
Strontium	Tin	Gold
Calcium	Lead	Iridium
Magnesium	Hydrogen	Rhodium
Aluminium	Antimony	Osmium
Chromium	Bismuth	

*Non-Metals —*

Silicon	Selenium	Bromine
Carbon	Phosphorus	Chlorine
Boron	Sulfur	Oxygen
Nitrogen	Iodine	Fluorine

Four important consequences follow from the above statement of fact and hypothesis.

(a) **Displacement Series.** If a metal of a certain solution tension be placed in a solution of the salt of a metal of lesser solution tension then the latter metal should precipitate and its place in solution be taken by the more "active" metal. We find, in fact, that any metal in the series will displace the metals which follow it from solutions of their salts at a rate which increases the farther apart they are in the series. Thus



In this relation, then, we find the explanation of the removal of



hydrogen from water and the acids by those metals which precede hydrogen\* in the series. (See pp. 54, 55.)

(b) **Voltaic Cells.** If any two members of the electromotive series are brought in contact with an electrolyte and connected externally by a conductor of the first class we have what is known as a voltaic cell, the electromotive force of which should be, according to the considerations above stated, the difference of the single potentials of the electrodes and a current should flow so long as these potentials can be maintained. Thus, for example, the electrode potential of zinc, in terms of hydrogen as zero, is  $-0.493$  volt, when zinc is immersed in a normal solution of zinc sulfate. The potential of copper in copper sulfate is  $+0.606$  volt. A cell made up of copper in copper sulfate and zinc in zinc sulfate should have an electromotive force of  $0.606 - (-0.493) = 1.099$  volts. This is the Daniell cell and the direction of the current is ordinarily indicated as illustrated in Fig. 92.



FIG. 92.

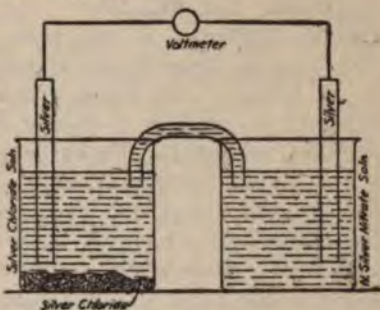


FIG. 93.



FIG. 94.

In a similar manner all the pairs may, with suitable arrangement, produce cells the electromotive force of which is the sum of the single potentials. A table of these potentials is found in Chapter XXVIII.

(c) **Concentration Cells.** If we consider electrode potentials as due to the equilibrium between the tendency of the ions in solution to precipitate and of the electrode to ionize it follows that the more concentrated the solution of metallic ions in which the same metal

\* It is to be noted that while hydrogen in the periodic system is an "Ishmael," in this relation it finds a real place. In the non-metal series it is to be noted that those elements highest in the series are in general most readily displaced. (See also the halogen family, Chap. X.)

is used as an electrode the smaller should be the electrode potential. This is apparently the case and advantage can be taken of it to produce what are called **concentration cells**. Thus, if zinc is placed in a solution of zinc sulfate of normal concentration, its E. M. F. is 0.493, while in a tenth normal solution its E. M. F. is 0.551. If now a cell is made up of these two factors connected as in Fig. 93 a current of  $0.551 - 0.493 = 0.058$  volt will be produced and will continue to flow until by deposition of zinc from the stronger solution and solution of zinc from the electrode in the more dilute solution the two solutions become of equal concentration, when, since  $0.493 - 0.493 = 0$ , no more current flows. A curious example of this relation may be demonstrated by partially immersing a stick of tin in a concentrated solution of tin chloride and superimposing upon the concentrated solution a very dilute solution of the same salt. The tin stick thus forms both electrodes and a deposit of tin forms on the lower end of the stick and solution takes place from the upper portion. See Fig. 94.

d. **Decomposition Voltage.** If we pass an electric current through an electrolyte we observe the separation of materials at the electrodes, if the latter are insoluble, and the minimum electromotive force required to produce a steady electrolysis is known as the **decomposition voltage** or **discharge potential** of an electrolyte. From the above considerations it ought to consist of two factors, the potential required to overcome the ionization tendency of the material of which the cation is composed and that of the anion. The decomposition potential of certain electrolytes is indicated in the table, p. 504, Chapter XXVIII, and also a table of the discharge potentials of certain ions. A study of these tables will reveal the fact that if we pass a current through a **mixture** of salts of the metals we should be able to secure, by proper regulation of the voltage, potentials at which one alone of the metals will be deposited. For example, if lead nitrate and silver nitrate be electrolyzed at a potential of more than 0.70 volt, and less than 1.52 volts, silver only will be deposited. This means of separation of the metals is known as **electro-analysis** and is used extensively, particularly in the separation of copper in pure form (see metallurgy of copper).

8. **Valence Relations.** The maximum valence of a metal is in general the same as the number of the group of the periodic system to which it belongs, and hence with the different metals we have a variation of from one to eight. An exception to this



statement is found with copper and gold, which, while belonging to the first group, show a maximum valency of two and three respectively. In the second group we have no variation from bivalency except with mercury, which is univalent in certain compounds as well as bivalent in others. With the metals of the other groups we find varying valency to a greater extent. As a rule the commoner compounds of the metals of the third group are those in which the element is trivalent. In the fourth group the metals of larger atomic weight are usually bivalent instead of tetravalent. The metals or metal-like elements of the fifth, sixth, seventh and eighth groups show in different compounds variations of valence varying from one to the maximum for the group. The more usual valencies are 3 and 5 for the 5th group, 2, 4, and 6 for the sixth, 1, 3, 5, 7, for the seventh and 2, 4, 6, 8, for the eighth (see Theory of Valence, p. 627).

**Uses of the Metals.**—The metals are used to such an extent and in such variety as to make a classification difficult, but the following types of application may be distinguished.

1. **As Structural Material.**—This term is usually used only when large structures such as buildings are considered, but may be extended to cover all sorts of mechanical devices. The metals most used in this manner are iron, in its various modifications, and copper, though many other metals are also used for special purposes. This use of these metals is too familiar to need detailed discussion.

2. **As Alloy Components.**—As already mentioned, alloys find many and important applications, and many metals are employed as components. Those most frequently so employed are copper, zinc, lead, tin, silver, gold, bismuth, and antimony (see Appendix).

3. **As Conductors.**—In modern times electricity plays so important a part in our activities that huge quantities of metals are employed in its conveyance, control and uses. Of the metals so employed copper is by far the most important, but aluminium, silver, tungsten, and manganese also find very important applications.

4. **As Protective Coverings for Other Metals.**—Various other metals are used in this connection, but the most extensively employed are zinc and tin. These are ordinarily employed to protect iron and the combination of iron coated with tin is known as "tinplate" while iron coated with zinc is known as "galvanized

iron." In lesser amounts "plated" materials are made, using nickel, copper, gold or silver as the surface metal. In most cases where the latter metals are used the protective value of the external metal is less important than the improved appearance so secured. Mellor rather picturesquely describes this function of metals as "sacrificial" where the purpose of one is to protect the other from corrosion.

**5. As Fuels or as Reducing Agents.** — Not infrequently metals are used as means of preparation of more valuable metals, from their ores. In this connection they may serve, not only as a reducing agent, but sometimes as well to furnish the needed temperature to convert the metal produced to liquid form. In some instances the convenience of utilization overweighs comparative costs. An example is furnished by the use of aluminium in incendiary bombs, as used in Zeppelin warfare, where molten iron is prepared at the cost of oxidized aluminium.

**6. As Components of Salts.** — Most extensive of all uses of the metals is that where they form portions of useful compounds. In many cases these compounds are found ready formed in nature and are utilized either with or without modification, but in many cases the metals are prepared from natural compounds and subsequently converted into more valuable compounds. Examples are furnished by the conversion of lead to the carbonate or acetate, sodium to sodium acetate, etc.

**Compounds of the Metals.** — The compounds of the metals, vast in number and importance, can be considered, with some exceptions, under the heads of oxides, basic and acid, hydroxides, and salts. The discussion of these forms an important portion of the following chapters. The exceptional compounds such as hydrides, carbides, silicides, etc., will be discussed when their more important representatives are encountered. (See potassium hydride, calcium carbide, iron silicide, etc.) Some general relations should be here pointed out.

**Oxides.** — In general, oxides of metals are prepared by direct combination with oxygen or by decomposition of hydroxides, nitrates or carbonates. The stability of these oxides is, in general, in inverse order to the position of the metals in the electromotive series, and the oxides of those in the lower portion of the table are unstable at room temperature, though absolute regularity in this



respect is not observed. The oxides are usually insoluble in water but those of the elements highest in the electromotive series react with water to form soluble bases. The most strongly basic oxides are those of univalent metals and this basicity is less, not alone with increasing valency of the different metals, but also decreases with increase of valency of a given metal, so that many oxides are amphoteric or even acidic.

**The Hydroxides.**—The hydroxides are not only made by reaction of the metals or oxides with water, which occurs only with the metals highest in the series, but more frequently by double decomposition of the salts by bases, *e.g.*,  $\text{CuSO}_4 + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + \text{Na}_2\text{SO}_4$ , or by hydrolysis of salts as  $\text{Al}_2(\text{CO}_3)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2\text{CO}_3$ . All the hydroxides except those of the alkali metals (*q.v.*) are decomposed at or below red heat forming water and the oxide, or water, oxygen and the metal. In many cases the hydroxides are unstable even at room temperature (*vide* mercury, silver, etc.). When decomposition of hydroxides by heat is effected it may be "stepwise," *e.g.*, lead hydroxide by decomposition may give  $x\text{Pb(OH)}_2 \rightarrow \text{Pb}_2\text{O(OH)}_2 \rightarrow \text{Pb}_3\text{O}_2(\text{OH})_2 \rightarrow x\text{PbO}$ . This type of decomposition is analogous to the formation of ortho-, pyro- and meta-acids from the normal type (*cf.* p. 304). The hydroxides of the metals are of varying solubility, but it is so slight in all normal hydroxides of the metals except those of the alkali and alkaline earth metals that they are considered insoluble. A table of solubilities (see p. 397) includes the more important hydroxides.

**Salts.**—The general statement may be made that we *may* have the salt of any metal with any acid radical. It is also frequently possible to prepare with each acid radical as many salts as the metal possesses variations of valency. By no means have all such salts been prepared. There are also possible mixed salts of the polybasic acids. The existence of double and complex salts have already been mentioned (see p. 181 and p. 389). Acid salts and basic salts and hydrates are also numerous. (See p. 181 and p. 81.) The methods available for making salts have been classified on p. 182. The salts may be classified according to the radical present and the most important from the standpoint of utility and frequent occurrence are the halides, sulfides, sulfates, nitrates, carbonates and silicates. Their solubility in water has a very important bearing on

both their utilization and the methods employed for their separation and identification. A table of solubilities of certain compounds is presented on the opposite page. The metal compounds may be very roughly divided into the two groups, soluble and insoluble, and the following general rules are useful.

1. All potassium, sodium, caesium, rubidium, and ammonium salts are **soluble** in water **except** the chlorplatينات and acid tartrates of potassium, caesium, rubidium and ammonium, and the silicofluorides of sodium and potassium and the aluminofluoride and pyroantimonate of sodium.

2. All chlorides, bromides and iodides are **soluble** in water **except** those of silver, lead and mercury (ous).

3. All chlorates, nitrates and acetates are **soluble** in water. Basic salts are usually less soluble than the normal or acid salts.

4. All sulfates are **soluble** in water **except** those of barium, strontium and lead. Silver and calcium sulfates are fairly insoluble.

5. All carbonates, phosphates, borates, oxalates and arsenates are **insoluble** in water **except** those of the alkali metals, but are soluble in dilute acids.

6. All sulfides are **insoluble** in water **except** those of the alkalis. The sulfides of the metals of amphoteric character are frequently hydrolyzed by water.

7. All oxides and hydroxides are **insoluble** in water **except** those of the alkali and alkaline earth metals. The oxides of these react with water to form hydroxides.

The above are useful rules, despite their approximate character and the fact that they cover only a few types of salts.

**Analytical Groups.**—The relative solubility of salts and hydroxides in water and their varied behavior with reagents is the basis of the mode of separation and identification known as qualitative analysis of the metals. The method of grouping varies somewhat but the following is a representative system. The metals ordinarily considered "common" are printed in "black-faced" type, and the rare metals in "italic" type.

1. Metals the chlorides of which may be precipitated from solution as chlorides in slightly acid solution. **Silver, lead, mercury (ous) thallium.** Certain other metals in the form of acid radicals, or anhydrides, may also become insoluble under such conditions, viz.: *molybdenum, tungsten, tantalum, and niobium.*



## Solubility of Bases and Salts in Water at 18°

(Taken, with permission, from "Inorganic Chemistry," Alexander Smith, p. 544.)

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.016 0.010	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.04 0.06	0.04 0.015	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.5	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.035 0.01	0.006 0.017	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.02
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 0.02	0.012 0.001	0.0016 0.02	0.0076 0.014	0.005 0.05	0.07 0.003
NO <sub>3</sub>	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO <sub>3</sub>	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO <sub>3</sub>	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO <sub>3</sub>	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.014	0.059 0.016	0.05 0.001	0.25 0.057	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.03
OH	142.9 18	116.4 21	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.02	0.05 0.05	0.01 0.04
SO <sub>4</sub>	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.023 0.010	0.011 0.06	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.013
CrO <sub>4</sub>	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.015	0.006 0.01	0.038 0.015	0.12 0.006	0.4 0.03	73.0 4.3	..... .....	0.02 0.05
C <sub>2</sub> O <sub>4</sub>	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.02	1.48 0.030	0.0086 0.038	0.0046 0.026	0.056 0.043	0.03 0.0027	0.05 0.04	0.015 0.05
CO <sub>3</sub>	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.01	4.95 0.10	0.0023 0.011	0.0011 0.07	0.0013 0.013	0.1 0.01	0.0047 0.037	0.01 0.03

The upper number in each square gives the solubility in grams per 100 cc. of water of the compound of the metal at the head of each column with the ion indicated in the margin. The lower number is the molar solubility.

The following are the solubilities (number of grams in 100 cc. water at 18° of two additional insoluble substances and of three acid salts:

Mercurous chloride, 0.02	Sodium bicarbonate	9.6
(molar sol'ty, 0.01)	Potassium bicarbonate	26.1
Mercuric iodide, 0.04	Potassium bisulphate	50.0
(molar sol'ty, 0.01)		

2. The sulfides of certain metals are insoluble in dilute acids and hence precipitation of them by hydrogen sulfide is possible. This group includes **mercury (ic) bismuth, copper, cadmium, arsenic, antimony, tin, palladium, gold, platinum, osmium, rhodium, ruthenium, iridium, germanium, selenium, and tellurium.**

3. The sulfides of certain metals are insoluble in neutral or alkaline solutions, or are hydrolyzed by water giving insoluble hydroxides and are soluble by dilute acids. In this group are included **iron, nickel, cobalt, aluminium, chromium, manganese, zinc, titanium, zirconium, uranium, indium, gallium, vanadium, beryllium,** and the whole group of elements known as rare earths (*q.v.*).

4. Four metals which do not furnish insoluble chlorides, hydroxides or sulfides are precipitated from neutral or alkaline solution by ammonium carbonate. These are **barium, strontium, calcium, and radium.**

5. A few elements do not furnish insoluble salts of any of the above types. These are **sodium, potassium, magnesium, lithium, rubidium, caesium,** and the "hypothetical metal" **ammonium.** It will be noted that in the above list are included some elements usually classed as non-metals. It should be expected from the principle of continuity that such cases exist.

The more detailed study of these relations is ordinarily pursued as a separate branch of chemistry, **qualitative analysis.** Certain general relations of each of the above groups and subdivisions of them will find place in the following chapters. The general classification will, however, be the grouping offered by the **periodic system.**

**Exercises.** — 1. The term "acidic" is frequently used in contrast with the term "basic." Explain and distinguish between the terms "base" and "basic."

2. Classify all the facts about metals which can be related to the electromotive series.

3. Make a list of all the metals employed for any purpose in your home and arrange them under the heads, "common," and "rare."

4. By examination of the subsequent chapters prepare a list of five metals which are prepared by the process of "smelting" with carbon.

5. Under certain conditions a metal of lesser solution tension



may partially displace one of slightly greater tension. On the basis of the law of chemical equilibrium, can you detail the conditions and explain why it should be possible?

6. Using a sheet of coördinate paper plot on the horizontal axis the atomic weights of the elements and on the perpendicular axis the specific gravities. (The values will make a more satisfactory curve if the atomic weights are divided by 10 and 1 mm. on the paper is then used for each unit.) Connect the points located by a curve and note its character. What relations are brought out by this curve?

7. Define the terms, light metals, heavy metals, alkali metals, noble metals, base metals, non-metals, metals, metalloids. Why is the division of the elements into metals and non-metals not a wholly satisfactory classification?

8. Review the chemical behavior of antimony and its compounds and itemize its metallic and its non-metallic characteristics.

## CHAPTER XXIII

### GROUP I—SUB-GROUP A

**General.**—The metals of group I, like the elements of every group, are divided into two sub-groups. Were the periodic system perfectly satisfactory as a means of classification we would expect from comparison with other groups that sub-group *A* would consist of lithium, potassium, rubidium and caesium, while sub-group *B* would be represented by sodium, copper, silver, and gold. It is recognized, however, that sodium is chemically and physically so closely related to potassium that this subdivision is not advantageous. We shall therefore include sodium with sub-group *A*, and also discuss in the same connection the remarkable radical, ammonium, which is chemically closely related with these metals.

The metals of the sub-group are very similar in their physical and chemical characteristics and are called the "alkali family." The term "alkali" is derived from the Arabic and originally referred to the ashes of saltwort. These consist largely of sodium carbonate and the term came to be used to describe those substances which had analogous properties. The term alkali has had varying uses in chemistry. Thus, the earlier chemists used the term "**fixed alkali**" for both sodium and potassium carbonates, and "**volatile alkali**" for ammonium carbonate. In general, potash, or potassium carbonate, is found in the ashes of plants and it is therefore sometimes called "**vegetable alkali**" in contrast with "**mineral alkali**," or sodium carbonate. In 1755, Black demonstrated the difference between the carbonates and oxides of certain metals, the former known as "**mild**" and the latter as "**caustic**" alkalies. (See Alembic Club Reprints, No. 1.) The term "**earth**" was used by the alchemists for such substances as were not calcined by heat and were insoluble in water, but certain of these were somewhat similar to the alkalies and hence known as "**alkaline earths**." The term alkali now ordinarily refers to the strong bases represented by the hydroxides of the metals of this group or their salts which are readily hydrolyzed in solution. (See Chap. XXVI.)



The metals of this sub-group are all soft and readily cut with a knife. The fresh surfaces are of brilliant metallic luster but tarnish quickly, through oxidation, on exposure to the air. This reactivity with oxygen is most marked with caesium and least with lithium and in general the same order holds with respect to other chemical properties. The metals all react with water, lithium least rapidly, giving hydrogen and hydroxides which are extremely active and stable bases, *i.e.*, these hydroxides in aqueous solution are highly ionized. The dry substances do not yield water when heated, as do the hydroxides of all other metals. All the metals are univalent in all their compounds and all form hydrides which are readily decomposed by water. They form salts with the acids which are soluble, as a rule, and the varying solubility furnishes means of separation from each other. While thus the members of the group are strikingly similar in chemical behavior, each has its own individual characteristics and these are sometimes not such as are to be expected from their positions in the periodic system. These variations are more frequent with lithium and sodium than with the other three. Thus, the hydroxide of lithium is by far the least soluble of the hydroxides, and its phosphate and carbonate are markedly more insoluble than those of the others. Sodium shows an abnormally high specific gravity and many of its salts are not isomorphous with the corresponding salts of the other members of the family.

The symbol for sodium, Na, is derived from the Latin term, "*natron*" (soda), while that for potassium is from "*kali*" the German term for potash, and the names sodium and potassium were bestowed by Davy when the two metals were isolated. Lithium owes its name to its preparation from mineral matter (*λίθος* = stony). The names rubidium and caesium are derived from the most prominent lines in their bright line spectra (see Chap. XXV). The symbol Cs is interesting since at the time of its discovery, C, Ca, and Ce were already appropriated by carbon, calcium and cerium.

### SODIUM

**Occurrence.**—Sodium occurs in nature in huge quantities as sodium chloride (*cf.* p. 87). It is also abundant in the form of complex silicates (*cf.* p. 298). The sodium salts are utilized by sea plants in their anabolism, much as potassium salts are by land plants, and when these are burned the ashes contain large percent-

ages of sodium carbonate. Deposits of the so-called sesquicarbonate, trona,  $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ , occur in various localities. Borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , and Chile saltpeter,  $\text{NaNO}_3$ , are also of extensive occurrence. Cryolite,  $\text{Na}_3\text{AlF}_6$ , is a valuable mineral. (*Vide* soda and aluminium.)

**History and Preparation.**—Metallic sodium was first prepared by Sir Humphry Davy, in London, in 1807, by the electrolysis of slightly moist sodium hydroxide. This discovery, simultaneous with that of potassium, was an important event in chemical history, not only because of the remarkable and new properties of these metals, but because it indicated that the oxides, previously

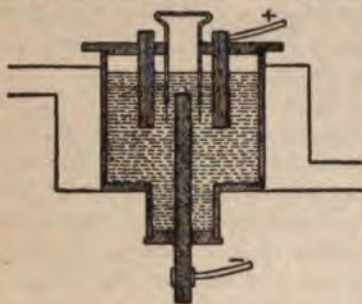


FIG. 95.

regarded as elements, were complex and that many others of the earths and alkaline earths were likewise probably complex. Also, it had wonderful effect in stimulating the use and study of the then new source of energy, the voltaic current, and resulted directly and indirectly in valuable development of chemical theory. (*cf.* Mellor, p. 350.) The present method used in its preparation, the Castner process (1890), is a modification of the process of Davy and is illustrated in Fig. 95. It may also be prepared by the electrolysis of sodium chloride or nitrate. (See also preparation of sodium hydroxide.) For many years it was chiefly prepared by reduction of sodium hydroxide by iron,  $4\text{NaOH} + 3\text{Fe} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{N}_2 + 4\text{Na}$  or by reduction of sodium carbonate by carbon,  $\text{Na}_2\text{CO}_3 + 2\text{C} \rightarrow 3\text{CO} + 2\text{Na}$ .

**Properties, Physical and Chemical.**—It is a silver white metal which melts at  $97.5^\circ$  and boils at  $742^\circ$ . Its vapor is dark green. It is soluble in liquid ammonia, forming a blue solution. Its vapor is monatomic. The metal dissolves readily in mercury to form an amalgam, with large evolution of heat, and if the percentage of sodium used is at all large, the mixture is solid and probably contains definite compounds of the two components. The metal reacts with moist air so readily that a freshly cut surface tarnishes almost instantly. To limit this action, it is fre-



quently kept under kerosene or other oil or in sealed vessels. It reacts so vigorously with water that the globule of sodium melts and floats on the surface, and spins rapidly, owing to the rapid formation of hydrogen and surface tension changes of the solution formed. The heat formed is seldom sufficient to ignite the hydrogen produced at the same time (*cf.* potassium), but if held in place by filter paper will do so. The globule not infrequently bursts with a violent explosion, so that the operation should be viewed from a respectful distance. The reaction is expressed,  $2\text{Na} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$ . If sodium is heated to from  $300^\circ$  to  $400^\circ$  in dry air, sodium peroxide is formed.

**Uses.**—Sodium is used in a variety of chemical processes in the laboratory, such as in drying organic substances which do not react with it and in which the hydroxide and hydrogen are both insoluble, *e.g.*, ether. Also in many organic syntheses, such as the building up of the hydrocarbon chains (*vide* organic chemistry). It is manufactured for use in the preparation of sodium peroxide and in the preparation of cyanides (*q.v.*). It was formerly used largely for the reduction of refractory ores of valuable rare metals, but the use in this manner has been discontinued in favor of the more effective and economical Goldschmidt process (*q.v.*).

**Compounds. The Hydride and Halides.**—Sodium when heated with hydrogen reacts to form the hydride  $\text{NaH}$ . The product is not only unstable at temperatures higher than  $350^\circ$  to  $400^\circ$ , but is exceedingly reactive with water. The hydride is a crystalline solid. The extremely important substance, **sodium chloride**, is already of necessity an old acquaintance of the student. It has been an article of commerce from time immemorial. Its natural sources have been attractive to animals and their neighborhood was consequently a "happy hunting ground" for savage and barbaric races. The vegetarian, whether animal or man, must have it as an article of diet, since the potassium salts of plants cannot apparently supply its place in the blood where it is kept constantly at one-third of its concentration in sea water. The civilized races demand purer salt than is ordinarily available in nature and though pure crystalline salt does occur, its purification constitutes one of the most ancient of chemical industries. All the processes, however varied, are essentially the fractional crystal-

lization of brines obtained either as sea water or by the solution, natural or artificial, of salt deposits. According to the degree of refinement, we have the various grades of salt. **Sea salt**, of course, contains all the salts found in sea water. If only the coarse salt crystals formed by partial evaporation of sea water by the heat of the sun are used we have what is known as "solar" salt. Table salt must be free from deliquescent substances, especially magnesium chloride, else it "cakes" in the salt cellars. Even pure sodium chloride is markedly hygroscopic. The perfectly pure salt is prepared most readily by making use of the solubility product of the system:  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ . If to a solution saturated with respect to salt but not its impurities, hydrochloric acid which furnishes a common ion, chlorine ion, is added, the pure salt separates out. Common salt crystallizes in



FIG. 96.

cubes, and a very interesting form is the hopper crystal shown in Fig. 96. Unless the crystals are formed slowly and with constant stirring they contain enclosed water, and on being heated explode because of internal formation of steam. This phenomenon is known as **decrepitation**. Salt crystallizes ordinarily without water of crystallization, but at temperatures below  $-0.15^\circ$  it crystallizes with two molecules of water:  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ . Its melting point is  $820^\circ$ . It volatilizes rapidly without decomposition at higher temperatures and boils at about  $1750^\circ$ . Its solubility is about 350 grams per liter and is not materially increased by increase of temperature. Sodium chloride tends to form double salts with the alkaline earth and earth chlorides, which tendency is by Remsen ascribed to the polyvalence of chlorine (see Remsen's double halide theory). Salt is used not only as an article of diet but in the preservation of meat and fish, in glazing pottery, drain-pipes, etc. It is the source of practically all other compounds of both sodium and chlorine. It finds almost countless other uses of a minor character. The other halide salts, the bromide, iodide and fluoride, are readily prepared but are not extensively used.

**The Oxides and Hydroxide.** — When sodium is burned in air under ordinary conditions a mixture of the oxide, peroxide and hydroxide is produced. If pure dry air is passed over heated sodium at about  $400^\circ$ , sodium peroxide is obtained which if allowed to react with warm water forms sodium hydroxide and



oxygen (*cf.* p. 30). The peroxide may be dissolved in *cold* water with but little decomposition, forming a hydrate,  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ . When this is treated with dilute acid hydrogen peroxide is liberated. This reaction is expressed  $\text{Na}_2\text{O}_2 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O}_2$  and is regarded as evidence that the peroxide has the structure  $\text{Na}-\text{O}-\text{O}-\text{Na}$  or  $\text{Na}-\text{O} : \text{O}-\text{Na}$ .

Sodium oxide,  $\text{Na}_2\text{O}$ , in pure form may be formed by treating sodium hydroxide with metallic sodium,  $2\text{NaOH} + 2\text{Na} \rightarrow 2\text{Na}_2\text{O} + \text{H}_2$ . It dissolves readily in water to form the hydroxide.

Sodium hydroxide has long been an important article of commerce because of its use in the manufacture of soap and because it is the cheapest form of strong alkali. It was for many years prepared almost wholly by treatment of sodium carbonate with slaked lime:  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + 2\text{NaOH}$ . This reaction goes nearly to completion in dilute solution by reason of the insolubility of the calcium carbonate. If sodium hydroxide of sufficient concentration be used the reverse reaction may be made to take place. Crude sodium hydroxide is produced using "trona," the natural form of the carbonate. If pure carbonate prepared by the Le Blanc or the Solvay process is used a purer form of hydroxide is obtained. (See also Mellor, p. 347.) It is sometimes purified still further by crystallization from alcohol and is marketed in stick form. Very pure hydroxide is made from metallic sodium and water. All these processes promise to be, or are, given up in favor of the electrolytic process which uses sodium chloride as a raw material. A number of patented devices for this method of preparation are on the market and it is impossible at present to say with certainty which device is the most efficient. One of the most interesting is shown in Fig. 32. It is the Castner-Kellner process, using mercury as a cathode. The amalgam so produced gives practically pure sodium hydroxide by reaction with water. (For details of various processes, consult Thompson's *Electro Chemistry*.) Sodium hydroxide is a white solid. It melts at a red heat. It deliquesces on exposure to moist air from which it also absorbs carbon dioxide, becoming ultimately converted to the carbonate. This substance then loses water and the mass gradually dries. It dissolves in water with evolution of heat and volume contraction. Vast quantities of sodium hydroxide are used in the preparation of soap and for other saponification processes; in the preparation of paper pulp (see also sodium acid sulphite); in the dyeing industry and for the refining of oils. It is also a very valuable laboratory

reagent. It is ordinarily known commercially as **caustic soda**. The oxide,  $\text{Na}_2\text{O}$ , has no commercial uses. The peroxide is, as has already been mentioned, a valuable means of obtaining oxygen, especially for pulmotors in mine rescue and other life-saving work. It is also used as a powerful oxidizing agent in laboratory operations.

**Sodium Carbonate.**—The carbonate was formerly prepared either by recrystallization of the naturally occurring trona, or by leaching the ashes of sea plants. When, during the Napoleonic Wars, France was cut off from her source of supply, a prize of 100,000 francs was offered for other means of preparation. This prize was won by Le Blanc (1794) whose method is as follows: Sodium chloride treated with sulfuric acid at high temperatures produces hydrochloric acid and sodium sulphate, known as "salt cake":  $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ . The acid was allowed to escape. The salt cake is heated with coal and limestone, the following reactions taking place:  $\text{Na}_2\text{SO}_4 + 2\text{C} \rightarrow \text{Na}_2\text{S} + 2\text{CO}_2$ , and  $\text{Na}_2\text{S} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaS}$ . This mass is known as black ash and is lixiviated with warm water and the solution separated from the undissolved calcium sulfide. The crude soda, formed by evaporation of the solution, is known as "soda ash." When recrystallized from water, with ten molecules of water of crystallization, it is known as "washing soda." If crystallized from water at or above  $35^\circ$ , it contains but one molecule of water,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , and is known as calcined soda. This process was the ordinary one during the earlier part of the 19th century, and it is interesting to note that the process involved the production of two undesirable by-products, the hydrochloric acid and the "tank waste," consisting of considerable percentages of calcium sulfide, and that the manufacturers had to be compelled by law to abate the nuisance of the escape of these substances, the former into the air, and the latter into the streams. During the latter half of the last century, with the development of other processes, this process was only enabled to compete by reason of the value of its by-products. The hydrochloric acid is absorbed by water and finds abundant market; the tank waste is treated with carbon dioxide and water, *i.e.*, carbonic acid, and converted into calcium carbonate and hydrogen sulfide,  $\text{CaS} + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{H}_2\text{S}$ ; the sulfide is burned in a limited air supply and the resulting sulfur marketed.

The **Solvay Process** was invented in 1891. By contrast with the fate of Le Blanc, who in the Revolution in France lost his patents and died insolvent and a suicide, the wealth accruing from



the Solvay process in the family of the inventor was so great that E. Solvay guaranteed \$10,000,000 of the indemnity laid upon Brussels in 1914, thus saving the city from destruction. The process depends upon the relatively small solubility of sodium bicarbonate. It is carried out by passing ammonia and carbon dioxide into a saturated solution of common salt, *i.e.*,  $\text{NaCl} + \text{NH}_4\text{HCO}_3 \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ . The bicarbonate is calcined to produce the carbonate:  $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ , and the resulting carbon dioxide may be again used in the process. The remaining carbon dioxide needed is produced by heating limestone:  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ , and the lime so produced is slaked and used to free the ammonia from ammonium chloride:  $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$ . The resulting calcium chloride has a small market value. It is an ideal commercial process since there are no waste products.

The **Cryolite Process** is also used to some extent. This consists in fusing cryolite with calcium carbonate:  $2\text{Na}_3\text{AlF}_6 + \text{CaCO}_3 \rightarrow 3\text{Na}_2\text{CO}_3 + \text{Al}_2(\text{CO}_3)_3 + 6\text{CaF}_2$ . This mass being leached produces a solution of sodium carbonate, and gaseous carbon dioxide. By hydrolysis of the aluminium carbonate,  $\text{Al}_2(\text{CO}_3)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{CO}_3 \rightarrow 3\text{H}_2\text{O} + 3\text{CO}_2$ , aluminium hydroxide is precipitated. The calcium fluoride is also insoluble.

The carbonate may also be prepared by passing carbon dioxide into electrolytic sodium hydroxide, and this process promises, through cheapening of electric power, to become a serious rival of the older processes. It will have been noted that the Solvay process produces the bicarbonate,  $\text{NaHCO}_3$ , as the primary product. This may also be prepared by passing carbon dioxide over the hydrated carbonate. The bicarbonate being anhydrous the water released from the decahydrate must be removed. This is accomplished by allowing it to drip through a grating on which the reaction takes place.

The properties of the carbonates have in part appeared in the discussion of their preparation. The common form of the carbonate is in large monoclinic crystals containing ten molecules of water,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . Since the vapor tension of these crystals is greater than the normal aqueous pressure of the atmosphere, the salt is efflorescent (*cf.* potassium carbonate). The salt which crystallizes from water above  $35.2^\circ$  is the monohydrate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , and at still higher temperatures this may be completely dehydrated. The relations are the same as illustrated

for sodium sulphate (see Phase Rule).  $35.2^{\circ}$  is the transition temperature from deca- to mono- hydrate. In aqueous solution, the carbonate is highly hydrolyzed, as mentioned in Chapter IV (hydrolysis).

The bicarbonate is an anhydrous salt and is very much less soluble than the carbonate. The reaction involved in its formation:  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons 2\text{NaHCO}_3 + 9\text{H}_2\text{O}$ , is reversible even in solution, so that on boiling carbon dioxide is evolved. On heating the dry salt the conversion to the neutral carbonate is readily effected. The bicarbonate is nearly neutral in solution, it does not affect even phenolphthalein, by reason of the very slight ionization of the ion  $\text{HCO}_3'$ , but evidently some hydrolysis takes place else the reverse reaction mentioned above would not occur.

← Sodium carbonate is used in vast quantities for making soap, glass (*q.v.*), for water softening, etc., and is also used as a cleansing agent both industrially and in the home. The bicarbonate when treated even with very weak acids is decomposed and carbon dioxide is liberated, and indeed twice the quantity which will come from the neutral salt containing the same quantity of sodium, hence the prefix *bi*. For this reason it is sometimes called *saleratus* (from *sal* = salt and *aer* = gas), though this term properly belongs to the corresponding potassium salt. It has been long used in cooking operations and is hence called "baking soda." As baking soda, its function is to evolve gas,  $\text{CO}_2$ , which, enclosed by the sticky dough (the stickiness being due to the gluten in the flour), expands when heated and so causes the dough to "rise" in the baking process. The liberation of the carbon dioxide, as well as the decomposition of the neutral carbonate which would otherwise be formed, is effected by means of sour milk, cream of tartar, alum, desiccated sodium aluminium sulphate, calcium acid phosphate, etc. These last are then the active factors, with the soda, of **baking powders**. The bicarbonate is also used in medicine as a mild laxative and ant-acid, and in effervescent drinks such as Seidlitz powders and bromo-seltzer.

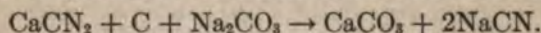
**The Sodium Sulphates.**—When anhydrous sodium sulphate is found in nature, it is called *thenardite*. It is found in certain strata in salt deposits. The sulfate is also found in solution in many mineral waters where its aperient effect frequently constitutes the sole medicinal value of the water. In the dry portions of the far west great deposits of the salt are found. These have been produced by the evaporation of lakes which formerly con-



tained the salt in solution. It is formed as the first step in the Le Blanc soda process and in the manufacture of nitric acid and in many other processes. It is usually a by-product rather than an object of manufacture. The decahydrate,  $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$  (Glauber's Salt), is crystallized from solution below  $32.4^\circ$ . The behavior of this salt with respect to solubility is fully discussed in Bigelow's *Theoretical Chemistry*, p. 340 (*q.v.*). The decahydrate is very efflorescent in ordinary air, being converted to the anhydrous salt. A heptahydrate,  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , is also rather readily prepared. The decahydrate reacts reversibly with hydrochloric acid (see p. 136) and if the crystals are treated with the concentrated acid, a marked lowering of the temperature is produced, hence the substances are used as a freezing mixture.

The bisulphate,  $\text{NaHSO}_4$ , is formed when salt is treated with an excess of sulfuric acid. It is converted on heating to about  $300^\circ$  to the pyrosulfate,  $\text{Na}_2\text{S}_2\text{O}_7$ , and this in turn, at higher temperature, to the neutral salt.

**Sodium Cyanide.**—This salt has recently become of importance because of its use in the cyanide process of gold extraction (*q.v.*). It is synthesized from ammonia, sodium and carbon. The steps of the process already given (p. 338) are carried out in one operation. In a suitably constructed furnace coke and sodium are heated in an atmosphere of ammonia, at  $500^\circ$ , until the amide is formed. The temperature is then raised gradually until at  $800^\circ$  the operation is complete and the molten cyanide drawn from the furnace. When cooled it is ready for the market without further treatment. The cyanide may also be made by fusing calcium cyanamide with coke and sodium carbonate:



**Other Salts.**—Among the many other salts of sodium which are important because of their uses may be mentioned the following: The nitrate,  $\text{NaNO}_3$ , especially important as a fertilizer; the polysulfide,  $\text{Na}_2\text{S}_x$ , used as an insecticide; the sulfite,  $\text{Na}_2\text{SO}_3$ , used as a raw material for the manufacture of the thiosulfate; the acid sulfite,  $\text{NaHSO}_3$ , used in the manufacture and bleaching of paper pulp and also in the "Bastol" process of manufacture of grain alcohol from wood; the thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , used as a solvent of silver salts by photographers and for many other purposes; the phosphates,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{NaPO}_3$ . The last of these is formed by heating "microcosmic salt,"

$\text{NaNH}_4\text{HPO}_4$ , and is used in the bead test in analytical operations. The tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7$ , is used in assaying and in welding, as a flux, in toilet preparations (borated talcum powders), as a preservative of foods, etc. The silicate,  $\text{Na}_2\text{SiO}_3$ , more or less pure, is used for fireproofing wood and other materials, as a binder for artificial stone (used for road metal), and for the preservation of eggs. As this partial list of salts will indicate, the satisfactory discussion of all the compounds is not possible within the limits of a text-book. When details concerning such compounds are needed the student should seek the handbooks such as those of Friend, Abegg, Dammer, and Roscoe and Schorlemmer.

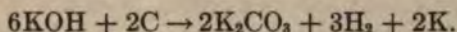
#### POTASSIUM

**Occurrence and Preparation.** — Orthoclase, one of the feldspars,  $\text{KAlSi}_3\text{O}_8$ , and mica,  $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$ , are common constituents of rocks. On weathering these give rise to soil (see p. 370) and plants use a portion of the potassium salts in their growth. These salts are returned to the soil when the plants decay. When the plants are burned, the potassium remains as the carbonate and may be leached out of the ashes. This was the source of the "lye" of our rural ancestors, which was used for making soft soap. The chief commercial sources of potassium are the salt deposits of Stassfurt, where it occurs as sylvite,  $\text{KCl}$ , and carnallite,  $\text{KMgCl}_2 \cdot 6\text{H}_2\text{O}$ . Potassium sulfate is also a constituent of salt deposits. When organic substances decay in the presence of basic materials, potassium nitrate is formed and this was formerly a great source of the salt, Bengal saltpeter  $\text{KNO}_3$ . One of the most remarkable sources of potassium salts is the kelp, seaweeds, which are said to contain 30–40 per cent of the weight of their dry residues as potassium chloride. (*Vide J. Ind. and Eng. Chem.*, Vol. 8, p. 568.) Some potassium salts are now obtained by the precipitation of the dust from the cement plants by the Cottrell precipitation method.

It is not essential to repeat in detail all the facts concerning potassium and its salts which have been taken up under sodium. The metal was first prepared by Davy by electrolysis and is now, but only recently, made chiefly by this process. Formerly the chief process was the reduction of potassium carbonate by carbon:  $\text{K}_2\text{CO}_3 + 3\text{C} \rightarrow 2\text{K} + 3\text{CO}$ . This method was not wholly free from danger, since the potassium formed tends to unite with carbon monoxide to form potassium carbonyl,  $(\text{KCO})_6$ , a violently explo-



sive compound. By Castner's modification, heating the hydroxide with a spongy mass of carbide of iron formed by heating pitch with iron filings, the formation of the carbonyl is thus avoided, since the reaction is:

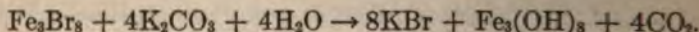


**Properties.** — The metal is silver white but tarnishes so quickly in air that the bright surface of a fresh cut almost instantly disappears. It melts at  $62.5^\circ$  and boils at  $760^\circ$ . Its specific gravity is 0.8621 at  $20^\circ$ . Its vapor is greenish and when incandescent gives a violet light (see flame colorations). The density of the vapor corresponds to that which would indicate monatomic molecules. It unites violently with the hydroxyl group from water and the heat liberated ignites the hydrogen evolved. Like sodium, it must be preserved out of contact with the air. It also unites readily with the halides and with various other elements with more vigor than does sodium. It is not used to any very great extent because of its higher cost than the similarly utilizable metal sodium. Its compounds, however, though possessing properties closely resembling those of sodium, are extensively used, since in many cases they cannot be replaced by the cheaper salts. In the following discussion, emphasis will be placed upon these uses and the properties which cause them.

**Compounds. Potassium Hydride and the Halides.** — The hydride, KH, is formed by heating hydrogen with the metal to about  $360^\circ$  and washing the impure product with liquid ammonia (see sodium). The chloride is found, as previously mentioned, in sea water, where it is present in much smaller proportions than salt and also tends so very much more readily to form very soluble double salts, that it crystallizes out only from very concentrated mother liquors. (See Mellor, p. 224 *et seq.*) The potassium chloride obtained from the upper layers of the salt deposits of Stassfurt not only are the chief source of this substance, but it in turn is used to prepare most economically nearly all the other potassium salts. The revenue derived from this source has been an important factor in German development, and more particularly, since potassium salts are an important factor in the fertility of the soils, relatively cheap potassium chloride has enabled Germany to make her fields so fertile that she is, in spite of her dense population, nearly a self-sustaining land.

She has emphasized this advantage by an export duty on the chloride and also by limitations on the quantity exported. The salt crystallizes in cubes not perfectly isomorphous with sodium chloride. The salt is less soluble in cold water than is common salt (28 : 35 at 0°) but more soluble in hot water (58 : 39 at 100°).

The bromide also crystallizes in cubes. It is obtained from potassium hydroxide treated with bromine or by treatment of iron filings with bromine and the product,  $\text{Fe}_3\text{Br}_8$ , with potassium carbonate:



It is used extensively as a nerve sedative, in the making of photographic plates (see photography) and in making printing papers of certain types and as a retarder in photographic development. It is a constantly used source of bromide ions in the laboratory in spite of the fact that sodium bromide is cheaper.

The fluoride occurs in two forms because of the complex molecules of hydrofluoric acid ( $\text{H}_2\text{F}_2$ ), viz.,  $\text{KHF}_2$  and  $\text{K}_2\text{F}_2$ . The former is a convenient source of pure anhydrous hydrofluoric acid since it can be decomposed by heat into the fluoride and the acid,  $2\text{KHF}_2 \rightarrow \text{K}_2\text{F}_2 + \text{H}_2\text{F}_2$ . It was the salt electrolyzed by Moissan to prepare fluorine (*q.v.*).

The iodide of potassium is formed as is the bromide and the crystalline cubes can be readily obtained in pure form. It finds extensive use in medicine, photography, and in the laboratory in spite of its high cost. Its solutions dissolve iodine in large amount, and undoubtedly form the compound,  $\text{KI}_3$ . This also finds use as a laboratory reagent and in medicine as a lotion.

**The Oxides and Hydroxide.**—The oxide is prepared by direct union of oxygen with the metal at or about 180° or by reducing the nitrate with potassium:  $2\text{KNO}_3 + 10\text{K} \rightarrow 6\text{K}_2\text{O} + \text{N}_2$ . The treatment which yields sodium peroxide (*q.v.*) gives with potassium an impure tetroxide,  $\text{K}_2\text{O}_4$ , a yellow solid, which may be obtained in pure form by melting potassium in an atmosphere of pure nitrogen, and while molten introducing oxygen so long as it is absorbed. The tetroxide reacts very violently with water to produce oxygen, hydrogen peroxide and potassium hydroxide. It is not certain that the peroxide,  $\text{K}_2\text{O}_2$ , has been prepared.

The hydroxide was formerly made wholly by double decomposition of lime with potassium carbonate. It is now prepared almost wholly by electrolysis. It is purified by the same methods



used for sodium hydroxide. It is a white solid which does not lose water even at a red heat. It is very deliquescent and extremely soluble in water, nearly 1500 grams per liter of water. Like sodium hydroxide, it has an exceedingly corrosive action on the flesh, and to this action is due the names caustic potash, and caustic soda. The reaction with the tissues is of the type of hydrolysis. It is more expensive than sodium hydroxide and hence not used so extensively. It is mainly used in making soft soap.

**Potassium Chlorate.**—With this salt the student is already familiar. It was formerly made by the process described on p. 197, but is now chiefly prepared electrolytically from potassium chloride. Recently, it has been demonstrated that practically pure potassium chlorate can be prepared by the electrolysis of the extract of kelp ash (*cf.* p. 410) (see a thesis by Henry Howard, University of Washington, 1915. See also Mellor, p. 287.). It is used in the preparation of oxygen, of fireworks, and of certain varieties of matches. Its most extensive application is in the making of chlorate powders which are finding extensive use as explosives. The reason potassium chlorate finds so much more extended use than the sodium salt is that the latter is much more soluble, the ratios being at 18°, 6.6 to 97.2, and hence the latter is difficult to separate in the pure condition. It is also highly hygroscopic, while the potassium salt is not. Potassium perchlorate is also prepared in some quantity and its formation has already been discussed (*cf.* Chapter X).

**Potassium Nitrate.**—This is in many respects the most useful of the potassium salts. Its presence in soils and as Bengal saltpeter has already been mentioned (see p. 283). The niter farms or the East India supply (see p. 283), furnished the world's needs until about 1854 when the huge quantities needed for powder in the Crimean and other wars brought forward the method of double decomposition of Chile saltpeter and potassium chloride:  $\text{KCl} + \text{NaNO}_3 \rightarrow \text{KNO}_3 + \text{NaCl}$ . In this case the mother liquor contains the desired salt since the potassium nitrate is so very much more soluble than the sodium chloride. The salt is anhydrous and readily forms large prisms of the rhombic system which decrepitate on heating, because of enclosed water, and melt at 340°. When heated to red heat, it evolves oxygen and forms the nitrite (*q.v.*). It is used chiefly in the formation of **gunpowder** (in which the sodium salt may not be used since it is deliquescent), which is manufactured by intimately mixing potassium nitrate,

sulfur and carbon in the ratio of 75 : 10 : 14. The ingredients are mixed wet and on drying about 1% of water remains. The high polish shown by the mixture is secured by revolving the granules in rotating drums. The reaction of the components of gunpowder on explosion are somewhat complex, but the general course is indicated by the equation:  $4\text{KNO}_3 + \text{S}_2 + 6\text{C} \rightarrow 2\text{K}_2\text{S} + 2\text{N}_2 + 6\text{CO}_2$ , and the smoke is due to the solid sulfide (see Explosives, Benson's Industrial Chemistry). The manufacture of gunpowder is now probably as extensive as it ever was, in spite of the modern use of "smokeless powders" which are much more powerful, because it is a slow-burning powder and gives what is known as a "lifting effect" to explosions in which it is a component rather than the shattering effect with the more rapidly explosive guncottons, nitroglycerine, gelatine, picric acid, and others of the large family of modern explosives. Its use in blasting powders for stumping and clay operations therefore continues. The nitrate is also used largely in the "corning" of beef.

**Potassium Nitrite.**—This salt is formed by heating the nitrate sufficiently, but the formation takes place more readily, as is to be expected from the principles of chemical equilibrium (*q.v.*), if a consumer of oxygen is also present. The reducing substance used is lead:  $\text{KNO}_3 + \text{Pb} \rightarrow \text{PbO} + \text{KNO}_2$ . This salt finds uses not duplicated by sodium nitrite, for example in separating cobalt from nickel by the double nitrite method (*q.v.*).

**The Carbonates.**—The carbonate and bicarbonate of potassium offer no points of interest different from those exhibited by the sodium salts except as follows: Potassium carbonate is exuded in the perspiration of herbivorous animals and is the partial cause of the continual dampness of the wool of sheep since it is so strongly deliquescent. The fatty material known as "suint," washed from wool, contains potassium carbonate and lanolin, a well-known drug. The chief use of the carbonate is in the manufacture of soft soap and hard, *i.e.*, infusible, glass. (See Glass.) The bicarbonate, the true saleratus, was formerly much used in cookery. The carbonate is used in the laboratory as a drying agent.

**Other Salts.**—Among the other salts of potassium of which space forbids discussion and yet of importance in several ways, are: potassium cyanide, already discussed (see p. 338), the cyanate,  $\text{KCNO}$ , the sulfocyanate,  $\text{KCNS}$ , the sulfate,  $\text{K}_2\text{SO}_4$ , the acid sulfate,  $\text{KHSO}_4$ , the pyrosulfate,  $\text{K}_2\text{S}_2\text{O}_7$ , the persulfate,  $\text{K}_2\text{S}_2\text{O}_8$ ,



the sulfide,  $K_2S$ , the polysulfide,  $K_2S_x$ , the pyroantimonate,  $K_2Sb_2O_7$ , the acid tartrate,  $KHC_4H_4O_6$ , known as cream of tartar, the sodium potassium tartrate,  $KNaC_4H_4O_6$ , known as Rochelle salts, the silicates, etc., etc. The student will observe the wide range of these compounds and recognize the fundamental importance of potassium in the chemical system. For details, consult such handbooks as Friend, Abegg, Dammer, etc.

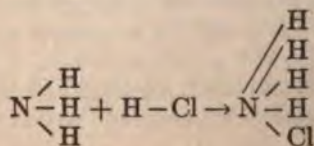
#### AMMONIUM

The relation of ammonia to the radical ammonium has already been pointed out (p. 267). The recognition of the metal-like character of the group and its relation in properties to the alkali metals we owe to Ampère (1816), though ammonium salts had been known for centuries before and ammonium amalgam (*vide infra*) had been prepared as early as 1808 by Berzelius and by Seebeck. The fact that the group of elements  $NH_4$  plays the part of a metal-like element in the formation of ammonium hydroxide and of salts has led to vigorous efforts to isolate the substance. These have been as yet without result and the nearest we have come to this result is the preparation of **ammonium amalgam**. This "compound" can be prepared by electrolysis of concentrated solutions of ammonium salts using mercury as a cathode. It may also be prepared by treating a dilute amalgam of sodium (about 1 per cent) with a concentrated solution of ammonium chloride. The reaction suffered to take place is,  $NH_4Cl + Na(Hg) \rightarrow NaCl + NH_4(Hg)$ . When the amalgam is prepared at very low temperatures it is a hard solid and even at  $0^\circ C$ . shows but little tendency to decompose. If the amalgam is treated at zero with salt solutions some of the metal of the salt is precipitated, for example,  $2(Hg)NH_4 + ZnSO_4 \rightarrow Zn(Hg) + (NH_4)_2SO_4$ . If the amalgam is allowed to warm up to room temperature the mass swells up to a spongy consistency of ammonia, hydrogen and the metal. Such reactions taken in conjunction with the general behavior of ammonium hydroxide and ammonium salts and with the existence of similar radicals such as that of the sulfonium bases  $S(R)_3OH$  (see organic chemistry) leave little doubt that the ammonium salts have the general formula  $NH_4X$ . That all such salts dissociate by heat into ammonia and free acid,  $NH_4X \rightarrow NH_3 + HX$ , is in accord with this conclusion.

**Compounds.**—Ammonium hydroxide has been discussed, p. 268, and it is only necessary to point out that since the solution

presents the system,  $\text{NH}_4\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3$ , its reactions are not due alone to the ions of the base but are at times due to the presence of the ammonia. (*Vide* complex salts of silver and platinum.) The oxide  $(\text{NH}_4)_2\text{O}$  has not been isolated.

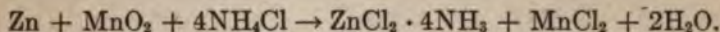
**The Ammonium Halides.**—**Ammonium chloride** is one of the most valuable of ammonium salts. The commercial name *ammoniac* is referred to on p. 263. It was formerly highly esteemed as a medicine and was mostly obtained from urine. Of recent years it is almost wholly obtained from "gas liquor" (p. 263 and p. 344) by passing the ammonia liberated from the liquor into hydrochloric acid, or by heating ammonium sulfate with sodium chloride,  $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + 2\text{NH}_4\text{Cl}$ . It is a white crystalline solid, forming either cubes or octahedra. It is most readily prepared in pure form by sublimation. The sublimed salt forms white fibrous masses. At  $350^\circ$  its vapor density is 29.04 ( $H = 2$ ), while its molecular weight should be 53.5. This relation is presumed to be due to dissociation;  $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$ , which if complete should give the value 26.75, i.e., the mean of the molecular weights of the acid, 36.5, and of ammonia, 17. At  $1040^\circ$  the density is 28.75. If the perfectly dry salt is volatilized it gives the value 53.5 (Baker, 1894). This is taken to indicate that traces of water vapor exercise a catalytic effect on the dissociation. The dissociation may also be inhibited by volatilizing the salt in an atmosphere of either ammonia or of hydrochloric acid. The clearing up of this relation had an important bearing on the acceptance of the validity of Avogadro's hypothesis as a valid criterion for relative weights of molecules and also as a final test in selecting atomic weights. With the development of the idea of valence, Kekule (1860), in order to avoid the assumption of varying valence of elements, considered ammonium and similar compounds to be "molecular." Thus ammonium chloride was assumed to be made of ammonia, in which nitrogen is trivalent and hydrochloric acid, the union being of a different sort than that between hydrogen and nitrogen. Although Thorpe and Victor Meyer and others showed this not a fruitful or valid assumption and that it is preferable to regard the structural relations as indicated:





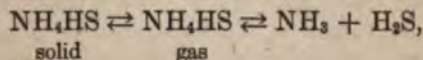
and so enforced the idea of varying valency in the case of nitrogen as well as of other elements; yet the classification "molecular compounds" persists and includes those substances in which the valence relation is either obscure or there are involved assumptions which most chemists are not agreed upon. (Examples of such compounds are hydrates, p. 82, nitrosyl compounds, p. 293, the double halides, p. 521, etc. See also Theory of Valency, p. 627.)

Ammonium chloride is used as a flux in soldering, where it acts most probably as a cleansing agent by reason of the successive reactions,  $\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$  and  $\text{M} \cdot \text{O} + 2\text{HCl} \rightarrow \text{M} \cdot \text{Cl}_2 + \text{H}_2\text{O}$ , and when all these factors are volatile or liquid at a red heat, or are soluble at lower temperatures, clean metal surfaces are provided antecedent to the soldering proper. (The same function is performed in the use of borax in welding, though for a different reason.) Ammonium chloride finds frequent laboratory application. The most extensive use is in the manufacture of electrical devices, the most important of which is the dry cell, of which upwards of 50,000,000 are made annually in the United States alone. These cells are composed of a carbon zinc couple with the carbon surrounded by manganese dioxide and the zinc with a paste of ammonium chloride. The reaction which takes place is the formation of  $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$ ,  $\text{MnCl}_2$  and  $\text{H}_2\text{O}$  probably as follows:



**Ammonium bromide and iodide** are white solids, the latter deliquescent and unstable. They both find application in photography and the iodide is what is known as "colorless iodine." The **fluoride** is unstable and by hydrolysis forms hydrofluoric acid. It may therefore be used to etch glass.

**Ammonium Sulfides.**—When ammonium hydroxide is saturated with hydrogen sulfide a soluble salt,  $\text{NH}_4\text{HS}$ , is formed. It may also be formed by mixing equal volumes of gaseous ammonia and hydrogen sulfide. It is unstable and the system is,

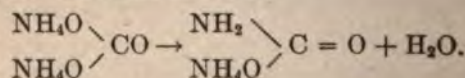


therefore when exposed to the air it completely decomposes by reason of the volatility of the gaseous products. If two volumes of ammonia and one of hydrogen sulfide are brought together the neutral sulfide,  $(\text{NH}_4)_2\text{S}$ , is formed. It may also be prepared

by saturating one-half of a given volume of ammonium hydroxide solution with hydrogen sulfide and adding the other half. It being the salt of a weak acid and a moderately weak base, is pretty largely hydrolyzed by water,  $(\text{NH}_4)_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NH}_4\text{OH} + \text{H}_2\text{S}$ . The ammonium hydroxide by decomposition gives rise to ammonia and the hydrogen sulfide to sulfur. If, therefore, ammonium sulfide is exposed to air ammonia escapes and polysulfides of ammonium are formed,  $(\text{NH}_4)_2\text{S}_x$ . The decomposition is also facilitated by action of light (see Actino Chemistry). The polysulfide is a very common and valuable laboratory reagent, being employed not only to precipitate the sulfides of the third group (analytical) metals, but also as a solvent for the sulfides of acidic character (sub-group B, Group II).

**Ammonium Carbonate,  $(\text{NH}_4)_2\text{CO}_3$ .**—This salt is one of the ammonium compounds present in gas liquor. The so-called "sesquicarbonate" is prepared ordinarily from calcium carbonate and ammonium sulfate by sublimation. It is, as so prepared, really a mixture of the bicarbonate  $\text{NH}_4\text{HCO}_3$ , and ammonium

carbamate  $\begin{matrix} \text{NH}_2 \\ \diagdown \\ \text{NH}_4\text{O} \end{matrix} \text{CO}$ , which is derived from the neutral carbonate by loss of one molecule of water,



The neutral carbonate may be prepared, as is the sulfide (*q.v.*), using carbon dioxide instead of hydrogen sulfide.

**Ammonium Sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .**—It is the cheapest of the salts of ammonium. It is formed by collecting the ammonia, distilled from gas liquor, in sulfuric acid. It is used in immense quantities as a fertilizer (upwards of half a million tons per year in the United States), and is the raw material for the preparation of liquid ammonia, aqua ammonia and the ammonium salts.

**Ammonium Nitrate,  $(\text{NH}_4)\text{NO}_3$ ,** is formed by neutralization of nitric acid with ammonia. It is a very interesting compound by reason of its utilization in the formation of nitrous oxide (*q.v.*) and as a constituent of the explosive known as **ammonite**, which is a mixture of 80 to 90% of this salt and 10 to 20% of dinitrobenzene or trinitrotoluene, or nitronaphthalene. The decomposition of ammonium nitrate is an exothermic process and when heated alone, as in the preparation of laughing gas, the reaction may



be explosive if large quantities are heated or if the temperature be unduly raised.

**Other Salts.**—The following salts of ammonium are also to be mentioned: "microcosmic salt,"  $\text{NH}_4\text{NaHPO}_4$ , used in making beads for the "bead test" (see p. 305); ammonium sulfocyanate,  $\text{NH}_4\text{SCN}$ , used as an analytical reagent for the detection of ferric ions; the cyanate  $\text{NH}_4\text{OCN}$  because of its spontaneous transformation to urea (see p. 339); the nitrite  $\text{NH}_4\text{NO}_2$ , because of its decomposition to nitrogen and water (see p. 259); the oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , used as a reagent for detection and estimation of calcium; the persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , used as an oxidizing agent; the chlorplatinate  $(\text{NH}_4)_2\text{PtCl}_6$ , an insoluble salt isomorphous with, and closely resembling, the corresponding potassium salt.

### LITHIUM

The element occurs widely distributed but does not usually occur in large quantities. The chief compounds are petalite,  $\text{LiAl}(\text{Si}_3\text{O}_8)_2$ , and lepidolite  $(\text{R}_3\text{Al}(\text{SiO}_3)_3)$ , where  $\text{R} = \text{Li, K, Na}$  and numerous other minerals, though the amount seldom runs over six per cent of the crude mineral. It is found in traces in the ash of many plants and that of milk and blood. It is presumably also present in traces in fertile soils. Traces are also frequently found in water from practically all sources. When present in any notable quantity the mineral water is supposed to have medicinal value. The element was first recognized in 1817 by Argyvedson, but was first isolated by electrolysis of its fused chloride by Bunsen, 1855. It is the lightest of the metals, not only floating upon water but upon the kerosene in which it is ordinarily kept out of contact with air. It is the least active of the elements of its sub-group but reacts with water to form the hydroxide. It forms with hydrogen a hydride,  $\text{LiH}$ , as do sodium and potassium. The most striking reaction is with nitrogen with which at red heat it forms the nitride  $\text{NLi}_3$ . Its salts differ markedly in solubility from those of potassium and sodium. The chloride,  $\text{LiCl}$ , carbonate,  $\text{Li}_2\text{CO}_3$ , and phosphate  $\text{Li}_3\text{PO}_4$ , are its most important salts. The first, the chloride, is soluble in amyl alcohol and in pyridene and may by this fact be separated from the other alkali halides. The phosphate and carbonate are characterized by marked insolubility in water.

### RUBIDIUM AND CAESIUM

In the examination of the residue from the water of the Durkheim spring by means of the newly invented spectroscope (*q.v.*), Bunsen and Kirchhoff, 1860, observed specially prominent bright lines in the spectrum which led them ultimately to the isolation of the salts of two new elements which have the atomic weights 85.5 and 132.8 respectively. The former, from two specially bright lines near the red end of the spectrum, was called rubidium (*rubidius* = dark red).

The latter, characterized by two bright blue lines, was called caesium (*caesius* = sky blue). The elements have since been found to occur in certain rare minerals (see p. 358, Mellor) and along with the other alkali metals in various silicates. Both elements, while thus rather widely distributed occur only in small quantities. They have as yet found no practical applications either as elements or in the form of their salts. Their chief interest is, then, purely scientific. Their modes of preparation, their properties and their compounds are analogous to those of potassium.

**General Relations of the Alkali Metals.**—A convenient method of comparison of the properties is by means of the following table:

	Lithium.	Sodium.	Potassium.	Rubidium.	Caesium.
Date of discovery.....	1817	1807	1807	1861	1861
Atomic weight.....	6.94	23.0	39.1	85.45	132.81
Specific gravity.....	0.534	0.9712	0.8621	1.532	1.87
Atomic volume = $\frac{\text{At. wt.}}{\text{Sp. gr.}}$ .....	13.1	23.7	45.4	55.8	71.0
Melting point.....	186°	97°	62.5°	38.5°	26.5°
Boiling point.....	1400°	877.5°	700°	696°	670°
Specific heat.....	0.941	0.293	0.166	0.0792	0.0483
Conductivity in reciprocal ohms per cubic centimeter at 0° 1.06 $\times 10^4$ (Landolt-Bornstein)....	11.7	22.3	14.3	8.62	5.52
Solubility of chlorides at 20° C. Per cent by wt. in 100 g. of solution.....	42.4	26.38	25.5	47.66	65.1
Solubility per 100 cc. of water at 0°.....	77.9	358.6	329.5	.....	.....
Equivalent conductivity at dilution of 1024 l. at 25°.....	116.1	126.3	147.8	151	151.7
Ionic mobility at 18°.....	33.4	43.5	64.6	67.5	68

**Ionic Relations.**—All five of the metals of this group furnish univalent ions when their salts are dissolved in water. There is considerable evidence that these ions are hydrated in solution and one set of the facts which indicate this is given in the preceding table. The conductivity of the ions is in inverse order of their atomic weights. This is an anomaly unless they are "loaded" with water. Washburn, Remy (see G. McPhail Smith, J. Am. Chem. Soc., **32**, 722, 1915), and others have accumulated evidence which led them to believe that the relative degrees of hydration are Li 24, Na 16.9, K 9.6, Rb 6.4, Cs 3.7. The salts of the metals



are separable from each other as follows: The dry chlorides may be treated with amyl alcohol which dissolves lithium chloride. The remaining chlorides may then be dissolved in water and the double chlorides of platinum,  $M_2PtCl_6$ , formed. Sodium chloroplatinate is soluble. The three remaining salts are ignited and so converted to chlorides and platinum. The mixed chlorides may be then treated with stannic chloride and the potassium chlorstannate,  $K_2SnCl_6$ , dissolved in water. The remaining stannates may be converted to the chlorides and treated with antimony trichloride. The caesium salt  $Cs_2SbCl_6$ , is precipitated. The sulfates of potassium, rubidium, and caesium may also be separated from each other by conversion to the alums (*q.v.*). The relative solubility of the alums being as 13.5 to 2.27 and 0.62 grams per 100 cc. of water they may be separated by fractional crystallization.

The most striking characteristics of the salts of the metals are their flame colorations and spectral lines. When the volatile salts are heated to such a temperature that the gases are incandescent, lithium salts color the flame crimson; sodium, yellow; potassium, violet; rubidium, red; and caesium, blue. Of course if the salt of more than one metal is present the flame color produced will be the resultant color of the mixture. If, however, the flame is examined, spectroscopically, characteristic lines are produced which are considered as means of absolute identification. The importance of the spectroscope is readily evident and when a few more relations of this sort have been met the subject will be more fully discussed. (See Chap. XXV.)

**Exercises.** — 1. Write the equations involved in the preparation of soap from olein (p. 362) and potassium hydroxide, and transformation to hard soap by treatment with common salt.

2. Make application of the "mass action" laws (p. 136) to the increase of yield of hard soap by use of an excess of salt.

3. Write all the equations involved in the preparation of sodium bicarbonate by the Le Blanc process, and of sodium carbonate by the Solvay process.

4. Write all the equations for the steps involved in the preparation of sodium carbonate, starting with the electrolysis of sodium chloride by the Castner-Kellner process.

5. Since sodium peroxide is neither volatile nor soluble without decomposition, why do we write the formula  $Na_2O_2$  rather than  $NaO$ ?

6. In terms of the kinetic molecular hypothesis explain the efflorescence of hydrated sodium sulfate and the deliquescence of potassium carbonate.

7. Write the equations involved in the preparation of sodium pyrosulfate from sodium hydroxide and sulfuric acid.

8. Make a list of the salts of sodium given in the text and arrange them in the approximate order with respect to their hydrolysis at equivalent dilutions. Give your reasons for the order.

9. Assuming two pieces of iron covered with magnetic oxide of iron, write the reactions taking place before welding when the white hot metal is treated with borax.

10. Write all the reactions involved in the preparation of potassium chlorate by electrolysis of potassium chloride.

11. Recalling that the decomposition of potassium chlorate by heat is an exothermic reaction, explain in detail why rapid heating or the heating of large masses may produce explosive decomposition.

12. Give detailed explanation of decrepitation.

13. Explain in detail why the failure of ammonium chloride to show a specific gravity of about 1.85 would tend to invalidate Avogadro's hypothesis were dissociation not probable.

14. Why are "molecular" compounds not assigned structural formulæ? Write a formula for hydrated copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , assuming a valency of four for oxygen where necessary, and give any reasons available for the formula written.

15. Using the mass action laws (p. 136), explain why ammonium hydrosulfide would be more stable in an atmosphere of ammonia than in air.

16. In preparing neutral ammonium sulfide why divide the quantity of ammonium hydroxide solution into two parts? Why is ammonium carbonate not formed in solution?

17. Given alunite,  $\text{K}(\text{AlO})_3(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , how would you expect to prepare potassium chloride from it?

18. Write all the equations involved in the separation of the alkali metals from each other as described on p. 421.



## CHAPTER XXIV

### GROUP I—SUB-GROUP B

THE members of this sub-group, copper, silver and gold, present but few features in common with sub-group A. They have many properties resembling those of the group VIII triads. The free elements are very inactive and hence are not readily tarnished in air. They are all univalent and the univalent compounds are of similar character. They may also manifest higher valency. The valence of copper is two in its commoner salts. Gold salts show a valence of three for the metal. A few compounds of silver have been prepared in which it is apparently either bivalent or trivalent. By strong contrast with the alkali metals the hydroxides are insoluble, unstable, and markedly less basic. It is an unfortunate weakness of the periodic classification that it does not anticipate such marked differences in properties. It also fails to point out the general similarity of properties of the compounds of copper with those of mercury.

#### COPPER

**Occurrence.** — Copper occurs in a very large variety of forms. It is native in several localities and native copper is occasionally found in large masses. The sulfide ores are numerous; the most important are chalcocite,  $\text{Cu}_2\text{S}$ , chalcopyrite,  $\text{CuFeS}_2$ , and bornite,  $\text{Cu}_5\text{FeS}_4$ . Both oxides are ores; cuprite, or ruby copper,  $\text{Cu}_2\text{O}$ , and melaconite,  $\text{CuO}$ . The basic carbonates, azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , and malachite,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , are important ores. The element also occurs in traces in the feathers of certain birds. In the blood of the cuttlefish copper is said to play the part iron plays in the blood of mammals.

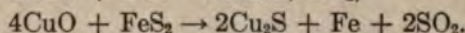
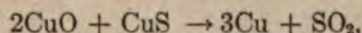
**History.** — Copper was known in prehistoric times, as the remains of prehistoric man show. This is but natural since native copper requires no smelting operation to prepare it and copper is readily worked into useful forms. The "bronze age," also pre-

historic, indicates that tin and also alloys of both metals were known in very early times. The metals and their alloys were known to both the early Greeks and to the Hebrews. The alchemistic symbol for copper was ♀, which was also the astrological symbol for the planet Venus. Since copper is readily precipitated from solutions of its salts by iron, the alchemists regarded its precipitation from blue vitriol solutions as an evidence of transmutation of metals. The real character of this interchange was first recognized by Boyle in 1661. The name seems to be derived as follows: To the Romans all kinds of bronze and copper were known as *aes*. The pure metal obtained from Cyprus was called *aes cyprium*, hence, came the term *cuprum* and the symbol Cu and the anglicised form, copper. In prehistoric times copper was evidently the metal most generally useful to man. It was utilized for the preparation of tools, weapons and ornaments. With the introduction of iron its relative importance decreased. In recent years the value of copper as an adjunct to electrical development has given it increased importance. The Great War has revealed its tremendous value in modern warfare. It is now second only to iron in metallurgical importance.

**Preparation.** — The processes used for winning copper from its ores have varied greatly at different periods and at the present are varied according to the type of ores employed and by local conditions at the point of manufacture. Only a bare outline of the more important processes can be given here. Ores carrying the native metal are ground to a fine powder and the gangue is washed away just as in the concentration of gold or other heavy metals or ores. The metal is then fused with a suitable fluxing material and the pure, or nearly pure, metal is drawn off in molten form. If carbonates and oxides are the ores employed the same general plan is followed except that coal or coke is used as a reducing agent. In case the ore is a sulfide the operation is more complex not only because of the presence of the sulfur, but because ordinarily enough gold and silver are present to render their extraction profitable. Arsenic, antimony, and other elements are also common impurities of the sulfide ores. The sulfide ores are usually concentrated until the copper content reaches 14 per cent. The concentrates are then roasted until the sulfide is converted to the oxide. The sulfur dioxide so produced is often utilized for the manufacture of sulfuric acid. The roasted ore is mixed with a quantity of raw ore,



or other sulfides. This mixture is then smelted in a low blast furnace along with enough fluxing material, limestone, and silica, to convert the gangue into a fusible slag. The oxide and sulfide ores react with each other to produce a mass of molten material which is known as copper "matte." The reactions may be roughly indicated by the equations:



The "matte" contains copper, cuprous sulfide, some iron and iron sulfide, besides any gold or silver present in the ores. It usually contains from 45 to 75 per cent copper. The molten matte is run into a converter (see Fig. 97) so arranged that air can be blown through the molten mass. The iron, sulfur, and other elements present are converted to oxides. The volatile oxides are of course volatilized. The iron oxide forms a fusible slag with the silica of the furnace lining, or with added silica. The air blast is stopped before appreciable quantities of copper are oxidized. The molten mass is drawn from the furnace and cooled. In cooling, the air and other gases occluded by the molten copper are given off and as the copper surface is rough, the cooled mass is hence known as "blister" copper. The blister copper is purified by one of the following methods:



Fig. 97.

(a) The copper is melted and stirred with poles of green wood which reduce any oxide present to metallic copper. When the operation is finished, the copper is cast in molds of any desired form. This is known as "poled" copper.

(b) If very pure copper is to be made either poled copper or blister copper castings may be dissolved and re-deposited by electrolysis. This is accomplished by hanging castings of the copper in a bath of copper sulfate solution which is acidified with sulfuric acid. These are made the anode of an electric circuit. The cathode consists of very thin sheets of pure copper. The current used is of very low voltage, but of very great density, *i.e.*, high amperage. In some cases a bath of ferric chloride and salt solution is used instead of copper sulfate. The copper is deposited in very pure form, the impurities being deposited as a sludge or "anode mud" at the foot of the anodes or remain in solution since the current strength employed is less than the decomposition potential of the salts (*cf.* Chap. XXVII). The attempt has been made to use

the electrolytic method upon copper matte and even upon copper ores but, so far as known to the author, with unsatisfactory results. The copper secured by the electrolytic process is 99.8 per cent pure. This high degree of purity is required when the copper is to be used for electrical purposes since very small amounts of foreign materials lower the conductivity of copper very markedly.

**Properties.**—Copper, free from tarnish, is a beautiful rose pink but soon acquires the familiar copper color on exposure to air. By transmitted light the color is green. Copper melts at  $1083^{\circ}$ . This is low compared with the melting point of iron, a fact which partially explains the early use of copper in metallurgy. A very interesting property of copper is its brittleness at or near its melting point, while it remains malleable and ductile at lower temperatures, even at the temperature of liquid air. The specific gravity varies somewhat with variation in the method of working the copper, but is very close to 8.8. It is one of the best of conductors of both heat and electricity. The ratio of the conductivity of copper to that of gold and silver is 63 : 45 : 67. If the item of cost be considered it is the best conductor for electrical purposes. In ordinary air copper is oxidized only very superficially, but in moist air a green basic carbonate is formed. This is frequently called "verdigris," though the true verdigris is a basic acetate of copper. Copper does not react with water or acids to displace hydrogen, nor does it displace metals above hydrogen in the electromotive series from solutions of their salts. Oxidizing acids readily attack it and the oxide formed is basic, *i.e.*, it reacts with the acids and forms salts. Sulfur also reacts readily with copper, especially at higher temperature. If acids, even weak acids, and air are simultaneously in contact with copper the oxide formed reacts with the acid to form salts. Since all soluble copper salts are very poisonous, this fact has an important bearing upon the use of copper in culinary utensils. The most valuable property of copper, aside from its conductivity, is the readiness with which it forms alloys (*vide infra*). The atomic weight of the element is 63.57 as determined by analysis of its oxides and other compounds. This figure also agrees well with that derived from its specific heat which is 0.0956. It also corresponds to the value obtained from the molecular weight of its volatile compounds and from its isomorphism with silver and gold salts. It has two equivalent weights which indicate a valence of one or two according to



conditions. It is one of the six metals which readily form addition products, as an ion, with ammonia. The monovalent series of salts are very similar to those of silver, though less stable and less easily formed. The divalent series are more analogous to those of bivalent mercury, iron, cobalt and nickel.

**Uses.**—Because of its inactivity with water, acids, and steam, (*cf.* electromotive series) it is used in a great variety of utensils, especially in manufacturing industries such as that of beer; as a covering for houses, ship bottoms, etc. It is also used in making plates in printing, engraving, etc., especially in electrotyping. Its use in manifold ways in electrical work is apparent to even the most casual observer. The alloys are very numerous and useful. On the whole, it is more generally used than any other metal save iron.

**Alloys.**—No other metal is so extensively used in the form of alloys as is copper, nor is there in any other case such a bewildering variety. A partial list only will be attempted. Copper coins are usually alloyed with 3 per cent tin and 2 per cent zinc. Gold and silver coins contain 10 per cent copper. Nickel coins contain 75 per cent copper and 25 per cent nickel. Brass, age old in use, is of somewhat varied composition. It is essentially  $\frac{2}{3}$  copper and  $\frac{1}{3}$  zinc, but also frequently contains tin and lead. Gunmetal, bell metal and bronze are essentially copper and tin though bronze usually contains some zinc and frequently also lead. Bronze is used in the making of statues, coins, ornaments, and instruments. Before the age of steel it was used for weapons and, especially, in castings. German silver contains copper, zinc and nickel in varying proportions, about 57 per cent, 19 per cent, 24 per cent, respectively. Manganese alloys are used for a variety of purposes, among them the manufacture of ship propellers. Manganese bronze contains up to 30 per cent manganese and the residue is mainly copper. Telephone and telegraph wires are frequently made of silicon bronze, which is essentially copper hardened and increased in tensile strength by small quantities of tin and silicon. Aluminium bronzes are of varying color and composition, that containing 95 per cent copper being very strong and light. It is used in yacht construction.

**Compounds.**—**Halides of Copper.** Cuprous chloride is formed by digestion of cupric chloride with hydrogen chloride in presence of

metallic copper. It is soluble in concentrated acid, but if the solution is poured into water a white precipitate of the cuprous salt is formed. Like all other copper salts the chloride unites readily with ammonia to form a complex ion, the compounds of which are soluble in water. The cuprous salt unites readily with carbon monoxide to form the compound cuprous carbonyl chloride,  $\text{CuCOCl}$ , which is soluble and has not been isolated. This reaction is extensively used in gas analysis for estimation of carbon monoxide. Cuprous chloride in solution is hydrolyzed by boiling water to cuprous oxide,  $\text{Cu}_2\text{O}$ , and is affected by light as is silver chloride. In the air, if moist, or in solution it oxidizes to the oxychloride, which is green in color. The solution in hydrochloric acid is probably a double chloride,  $\text{HCuCl}_2$ . The complex ion with ammonia is apparently  $\text{Cu}(\text{NH}_3)_2$ . Cupric chloride,  $\text{CuCl}_2$ , is the product of the direct action of chlorine upon copper and consequently of aqua regia upon copper. The salt crystallizes from solution to form a blue salt,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . The dry salt is yellow. The salt crystallizes rather readily as a double chloride with the alkali chlorides. There are two bromides and two iodides of copper. The cupric iodide is unstable and breaks down spontaneously to cuprous iodide and iodine.

**Oxides of Copper.**—Both oxides of copper are readily prepared. The lower oxide is red in color and is formed by gentle oxidation of the metal or by precipitation from cuprous salts by bases. The corresponding hydroxide is yellow and is unstable. It is temporarily formed in the determination of glucose by Fehling's solution (see any physiological chemistry text). The cuprous oxide is unstable in air, oxidizing more or less completely to the "ic" form. Cupric oxide is the final oxidation product of copper by heating in air, or is formed by heating the carbonate, nitrate or hydroxide. The latter dehydrates in the presence of water at  $100^\circ$  and the action is not appreciably reversible. The oxide is at room temperature somewhat hygroscopic, but does not give a basic reaction to water in which it is suspended. The oxide is readily reduced to metallic copper, apparently without stopping at the "ous" stage. It is therefore very useful in quantitative determination of carbon and hydrogen in organic compounds. Copper hydroxide, like aluminium, zinc, cobalt, and nickel hydroxides, is not precipitated by bases in the presence of many organic compounds, especially those containing "alcoholic hydroxyl" (see Chapter XX). The explanation which is most



probable is that the copper ion replaces the hydrogen of the hydroxyl group and thus copper ions as such do not exist in the solution. This reaction is the basis of reactions involved in the solution of cellulose in copper ammonia hydroxide solutions,  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ , and of the formation of Fehling's solution. The latter is a solution of copper sulfate, Rochelle salts (*q.v.*) and potassium hydroxide. It is much used in the estimation of glucose solutions, especially diabetic urine, since, when reduced to the cuprous condition, the copper hydroxide is no longer held in solution by the tartrate.

**Copper Carbonate**,  $\text{CuCO}_3$ , is not as yet obtained but, by reactions which might be expected to produce it, basic carbonates are formed. Two of these occur as minerals, as already mentioned. Precipitation reactions produce the substance having the composition of malachite,  $\text{Cu}(\text{OH})_2\text{CO}_3$ . This is the green material which so frequently stains the rocks where sulfide ores outcrop.

**Copper Sulfate**.—This is one of the longest known and most important of the copper salts. It is formed in nature in copper mines by the dripping of water over the sulfides and was collected and used by both the Greeks and Romans in medicine and in dyeing operations. It was known to the Arabian alchemists under the name of vitriol and the name is carried over to include a class of substances such as white vitriol, crystallized zinc sulfate, green vitriol, crystallized ferrous sulfate, etc. It is readily prepared by heating copper sulfide in the air and treating the mixture of copper sulfate and oxide so produced with sulfuric acid. It crystallizes from water as the pentahydrate, known as **blue vitriol** or bluestone. From hot concentrated sulfuric acid it may be crystallized in white needles. If copper sulfate solutions are crystallized along with the other vitriols, the heptahydrate,  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , is formed, which is isomorphous with them. The salt readily forms double sulfates with the alkali sulfates. These double salts are analogous to the alums (*q.v.*) though not isomorphous with them. Copper sulfate finds at the present time a wide range of uses in manufacturing other compounds of copper; in copper plating; in calico printing; in batteries; as a mordant in dyeing; and especially as a germicide and fungicide in horticulture.

**Other Compounds of Copper**.—The acetate of copper, formed by the reaction between vinegar, air, and copper, is the basic

salt, known as **verdigris**, and is used to some extent as a pigment. The mixed basic acetate and arsenite is known as **Paris green** and is used as a vermicide on plants. The arsenite, known as **Scheele's green**, was formerly much used in wall paper and other similar manufactures, but the poisonous nature of the material has forced a discontinuance of the practice.

The **ferrocyanide** of copper,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , finds use, not only in the detection of the element, but in the preparation of osmotic membranes. The **borate** and **phosphate** are used in beads for the detection of copper, the cuprous beads being red and the cupric blue. The **silicate** of copper in the "ous" condition is ruby red and is used for coloring glass.

### SILVER

**Occurrence.** — Silver occurs native, sometimes in large masses, but usually in small particles disseminated through a rocky matrix. Native silver is also usually alloyed with gold or with copper. Native copper and gold usually carry some silver. Silver also frequently occurs as the sulfide and is usually associated with galena, lead sulfide. The latter is at present the chief source of the silver produced. Smaller amounts of other argentiferous compounds also occur, such as **pyrargyrite**,  $\text{Ag}_3\text{SbS}_3$ . **Horn silver**, or silver chloride, is sometimes found in sufficiently large quantities to serve as a source of the metal.

**History.** — Silver has been known from the most ancient times. Job referred to silver and its use as money and for ornaments (Job 3: 15; 22: 25; 27: 16,17). The names used for it by both Hebrews and Greeks refer to its color and luster, and the alchemists referred to it by the term **luna** (the moon) and represented it by the crescent moon.

**Preparation.** — The earliest method of preparation of silver from ores was apparently the cupellation process in which the silver was reduced along with lead, and the lead driven off by oxidation and subsequent volatilization (mentioned by Solomon, Prov. 17: 3; 27: 21). Various processes and modifications have been used at various times but at present three methods are chiefly employed.

**The Cyanide Process.** — The ore is crushed to a fine powder, i.e., "stamped," and treated with a solution of sodium or potas-



sium cyanide. The double cyanide of silver,  $\text{KAg}(\text{CN})_2$ , is formed and dissolves. The reaction may be indicated:  $\text{Ag}_2\text{S} + 4\text{KCN} \rightleftharpoons \text{KAg}(\text{CN})_2 + \text{K}_2\text{S}$ . Since this action is reversible the change in the direction  $\rightarrow$  may be facilitated by removal of the potassium sulfide which is oxidized by free access of air. When a sufficiently concentrated solution is obtained, the silver may be recovered by precipitation by means of zinc.

**The Amalgamation Process (The Patio Process).**—This formerly much used method consisted essentially in converting the silver in the ores to a chloride by means of sodium chloride and dissolving the chloride in strong salt solution. From this the silver is precipitated by treatment with mercury, or mercury containing a little sodium amalgam. The silver amalgam is collected by washing, the excess mercury filtered off through canvas bags and the silver recovered from the amalgam by distillation.

**The Smelting Process.**—This is perhaps the most extensively used process. The ores, which usually are mixed copper, lead and silver ores, are heated with coke in low blast furnaces. The reduced silver alloys readily with lead and the alloy is drawn off from the bottom of the furnace and cast in molds. The lead "pigs" so formed are then desilvered by one of several processes. Of these the more extensively used are Pattinson's process and Parke's process. The former consists of melting the lead pigs and allowing them to slowly cool. The lead crystallizes out in practically the pure state, just as ice from saline solutions, until the percentage of silver rises to  $2\frac{1}{2}$  per cent, which mixture is a "eutectic" melting at  $303^\circ \text{C}$ . (See Chap. XIII, p. 253.) In practice the pure lead crystals are only removed until a residue consisting of 1 per cent silver is obtained. This residue is then "cupelled," i.e., the mass is heated in a slow current of air until the lead is converted into the oxide and volatilized. Parke's process consists in extracting the silver from the molten lead with zinc. Zinc not only alloys very readily with silver but the alloy is specifically lighter than lead so that it floats. It solidifies also more readily than the lead so that as the molten mass is allowed to cool a crust of zinc-silver (and gold, if present) alloy separates as a crust which may be skimmed off. The more valuable metals are obtained by volatilizing the zinc. Of course, the lead dissolves somewhat also in zinc, but the amount is small and is separated from the silver by cupellation.

**Properties.** — Pure silver is white and very lustrous if in large masses. In finely divided condition, like most metals, it is gray to black. Its specific gravity is 10.55. It is extremely malleable and ductile and hence capable of forming very thin sheets and very fine wire. It melts at  $960^{\circ}\text{C}$ . and boils at about  $2050^{\circ}$ . It may then be distilled by use of a blast lamp or by an electric furnace. Molten silver occludes about 22 times its own volume of oxygen which it again gives off on cooling. This is the cause of the crater-like eruptions which appear when molten silver cools. As a conductor of heat and electricity, silver takes a first place among the metals. If it be prepared in extremely finely divided condition, by sparking silver electrodes under water, or by reduction of silver nitrate by ferrous citrate or other reducing agents, it may be so obtained in colloidal suspension in various colored forms. (See colloidal solutions.)

Silver takes its place near the bottom of the electrochemical series and is classed as one of the so-called "noble metals." It is therefore unacted upon by acids which act only as such. It displaces only gold, platinum and palladium from their salts and is readily deposited by electric current of low E. M. F. (See Electromotive Series.) Air, moist or dry, has no effect on silver, but it unites readily with sulfur, hence silver utensils are readily tarnished by contact with perspiration or decaying albuminous or other bodies containing sulfur. Silver dissolves readily in nitric acid, owing to the oxidizing effect of the acid (*vide* nitric acid) and silver nitrate is formed. The solution becomes greenish in color if cold, owing to the presence of nitrous anhydride. This observation should be kept in mind since such coloration is sometimes taken to indicate the presence of copper, which is so frequently alloyed with silver. (See Alloys of Silver.) Silver reacts readily with the halogens, as well as with sulfur, and hence if heated halogen acids or hydrogen sulfide, the latter even in solution, are added to silver the corresponding salts are formed. The hydroxide of silver shows no tendency toward amphoterism. Silver vessels are therefore available for use with alkalis. Silver ions show, in common with a few other elements, a peculiar relation to ammonia, being capable of direct union to form complex ions of the formula  $\text{Ag}^{\circ}(\text{NH}_3)_2$ .

The atomic weight of silver, deduced from the analysis of its halogen salts, is 107.88, and this is in accord with the value derived from the specific heat of silver, which is 0.05625. The element is



univalent in almost all of its compounds. The salts are always represented by the simple formulæ, though, at least in organic solvents, polymerization undoubtedly takes place.

**Uses.** — Silver is a rather soft metal, and to increase its hardness it is alloyed with copper when used for coinage or other similar purposes. The degree of "fineness" is expressed in parts per 1000. American coin silver is 900 fine. British coin silver is 925. Silver ornaments and tableware are 800 or more. If silver containing copper is heated in the air, the copper is oxidized and may then be dissolved by acids, leaving the "frosted" silver effect. The so-called oxidized silver is produced by treating the surface of the silver with potassium acid sulfide, which produces a film of silver sulfide. Silver is used in making various compounds, which find more or less extended application in the arts. (*Vide infra.*) Silver is used for making high-grade mirrors, being deposited on glass (an invention dating back to 1300), from silver nitrate by glucose or other good reducing agent.

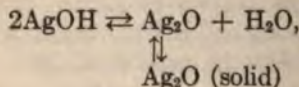
**Alloys.** — Silver is also used in a number of alloys, the most important being coin silver, as described above. Silver amalgam is, of course, important, since its preparation makes possible one of the methods of preparation of silver. The amalgam, together with tin, is used in filling teeth. Hard solder is made, using zinc, copper and silver in the ratio 4 : 2 : 5.

**Compounds. The halides.** — The chloride, bromide and iodide of silver are readily formed by precipitation of soluble silver salts with the soluble halides. Their insolubility is very great and increases in the order named above. The solubility of  $\text{AgCl}$  is about 1.6 mg. per liter and of the iodide about 0.06 mg. Silver chloride and bromide will therefore be converted to the iodide by standing in a solution of a soluble iodide. This is an interesting case showing how relative solubilities affect reactions, especially since chlorine and bromine will displace iodine from its salts.

Silver chloride dissolves in aqueous solutions of ammonia, forming the complex salts,  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . Though the dry salt absorbs ammonia apparently with the formation of two compounds  $\text{Ag}(\text{NH}_3)_2\text{Cl}$  and  $(\text{AgCl})_2\cdot 3\text{NH}_3$ , the bromide does not appear to form a similar compound, though the iodide does form  $2\text{AgI} \cdot \text{NH}_3$ ; however, the bromide dissolves in ammonia solutions,

while the iodide does not. Extremely remarkable is the fact that silver fluoride is a very soluble and deliquescent salt. The halides of silver readily form double salts with the alkali halides and these double salts are soluble (see Remsen's theory). Double salts are also formed when silver halides are treated with soluble cyanides or sodium thiosulfate. From the solution of the latter, crystals of the composition  $\text{Na}_4\text{Ag}_2\text{S}_4\text{O}_6$  may be obtained. The halides of silver when exposed to light suffer a change, which, while not perfectly marked, appears to be a decomposition into a lower halide. In the case of the chloride the white substance first becomes pink, then gradually darkens to black. Similar color changes are not observed with the bromide and the iodide. These interesting reactions of silver salts make possible the fundamental operations of photography and also aid in electroplating with silver (*vide infra*).

**Hydroxides and Oxides.** — When silver salt solutions are treated with hydroxides, a brown precipitate is formed which when dry has the composition  $\text{Ag}_2\text{O}$ . The double decomposition should give an hydroxide, but it appears to be unstable and to break down into the oxide and water. The aqueous solution doubtless contains the base, since it is distinctly alkaline and may be, and frequently is, used as a base. We are then dealing with the reversible system,



in which the major portion of the material is in the form of the solid oxide. This case illustrates very well the variation in the stability of the series of metallic hydroxides in which one finds at one extreme substances like silver and mercury of which only oxides exist in the dry form, and, at the other, substances like sodium and potassium hydroxides stable even at a red heat.

Silver oxide is soluble in ammonia, forming a base comparable in strength with potassium hydroxide. This is  $\text{Ag}(\text{NH}_3)_2\text{OH}$ . When a solution of this substance evaporates to crystallization, black crystals of "fulminating silver" are formed. It is extremely explosive when dry. Its composition is not certainly known but it is supposed to be silver nitride,  $\text{Ag}_3\text{N}$ .

Silver peroxide is formed by the action of ozone on silver and by the electrolysis of silver nitrate with strong currents, it appears on the anode in the form of black crystals.



crystals may be silver pernitrate, but, if so, the latter decomposes, giving the peroxide. Silver peroxide is not very stable and with water decomposes slowly, forming hydrogen peroxide. It probably has the constitution  $\text{Ag}-\text{O}-\text{O}-\text{Ag}$ , *i.e.*, is a true peroxide. The sub-oxide,  $\text{Ag}_2\text{O}$ , sometimes listed, is of uncertain existence.

**Silver Nitrate.**—The most important salt of silver is silver nitrate,  $\text{AgNO}_3$ . It forms colorless rhombic crystals which melt without decomposition at  $218^\circ\text{C}$ . It is frequently melted and cast in slender sticks, when it is known as **lunar caustic** and used as an escharotic in medicine. The dry salt is not changed by light, but if a solution in contact with reducing agents, such as cloth, etc., is allowed to evaporate in the light a black silver deposit is formed. It is consequently used in indelible inks.


**Other Salts of Silver.**—Of the numerous other salts of silver which find use for special purposes may be mentioned: **Silver nitrite**,  $\text{AgNO}_2$ , used for preparing standard nitrite solutions; the **carbonate**,  $\text{Ag}_2\text{CO}_3$ , which is formed by double decomposition either in solution or by fusion when silver salts are treated with carbonates and which in turn if heated, changes to the oxide and then to metallic silver. **Silver sulfate**,  $\text{Ag}_2\text{SO}_4$ , is but slightly soluble in water and finds certain minor uses for this reason. **Silver sulfide**,  $\text{Ag}_2\text{S}$ , is formed either by precipitation with soluble sulfides or by direct union. The various silver salts of phosphoric, arsenic, and chromic acids are useful in analytical work.

## GOLD

**Occurrence.**—Gold occurs in small quantities in many ores, particularly in the sulfide ores of copper, arsenic, antimony, etc., and in iron pyrites. **Sylvanite**,  $\text{Au}(\text{Ag})\text{Te}_2$ , is found in some localities. It is usually native either in a matrix of quartz or in fine grains, or large pieces, or nuggets, in alluvial formations. Native gold is seldom fine, being alloyed with silver, or other metals. It occurs in minute quantities in sea water (about  $\frac{1}{2}$  gram per ton or one part in ten million), and its extraction from this source has not proved profitable except to certain dishonest promoters. The distribution of gold is tremendous, it being found in practically all parts of the world. It is usually in such minute quantities that its extraction is not profitable. Even in those places where "pay streaks" are found, the quantity per ton of sand or rock is usually small.

**History.**—The use of gold for ornaments and as a medium of exchange goes back to prehistoric times. It is mentioned in the earliest of human writings and

is mentioned with appreciation by Job (28: 1; 31: 24). It was even considered by the Hebrews as one of the attractive features of the Garden of Eden (Gen.

2: 1, 2). The alchemistic symbol for gold was.  the same as the astro-

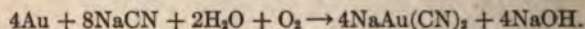
logical symbol for the sun. The transmutation of base metals into gold was the chief aim of the alchemists and their work with this object in view established many facts later incorporated into systematic chemistry. Other than in this connection the chemistry of gold has not played any important rôle.

**Preparation.**—The winning of gold from the alluvial deposits is called *placer-mining* and is usually accomplished by a washing process which depends upon the fact that its specific gravity, 19.3, is so much in excess of that of the other factors of the deposit. This washing may be done in a "pan," "cradle," or "sluice box." In each case the sand is agitated with water until the gold settles to the bottom and the lighter materials are floated off. In many cases mercury is placed in the sluice boxes to collect, by amalgamation, the fine particles of gold dust. In cases where large scale operations are possible the sand and gravel are washed into the sluice boxes by streams of water under high pressure. This is known as hydraulic mining. In case the gold is in veins of quartz rock, the rock is crushed to a fine powder by means of heavy "stamp" mills and the gold collected by one of the following processes:

(A) **The Amalgamation Process** is the oldest process and consists essentially in washing the powdered ore, as a "slime" with water, over copper plates amalgamated with mercury. The gold particles are retained by the plates and from time to time the plates are scraped and the mercury distilled. The gold remains in the retorts. This process is now seldom used, since a very considerable portion of the gold escapes into the "tailings."

(B) **The Chlorination Process** can be used, not only on quartz ores, but also on sulfide ores which have been roasted. The powdered ores are agitated with water in the presence of chlorine gas until the gold has been converted into the soluble chloride,  $\text{AuCl}_3$ . The solution is drawn off and treated with ferrous sulfate,  $3\text{FeSO}_4 + \text{AuCl}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{FeCl}_3 + \text{Au}$ , or with hydrogen sulfide. In the latter case the gold is obtained by roasting the precipitated sulfide.

(C) The most important process is known as the **Cyanide Process**. The powdered ore is leached by a dilute solution of a cyanide. Sodium cyanide is now usually employed. The process is facilitated by the presence of oxygen. The reaction is probably represented by the following equation:



From this solution the gold may be obtained by electrolysis or by precipitation by means of zinc shavings or by iron.

This process, devised in 1886, has had very important political results, since its use rendered the vast deposits of low-grade ore in the Transvaal immensely valuable, and consequently led to development by the English. This situation ultimately led to the Boer war and the formation of the United States



Africa. This confederation in turn is no mean factor in the great war in progress when this was written.

Gold is also obtained by many smelting processes as previously indicated (see preparation of copper and silver). However obtained, it is seldom free from silver or base metals, and must be **refined**. This may be accomplished by one of two methods:

(A) The cupellation process is the oldest, probably, of metallurgical processes other than those involved in working copper and iron. In any case it antedates exact historical knowledge. Gold is melted with lead and enough silver to make the silver-gold ratio in the resulting mass at least 3 to 1. The lead solution is then "cupeled" by roasting in a furnace in a shallow bone ash crucible, called a cupel. (See Fig. 98.) The lead is oxidized and a part of it, with other base metals, volatilizes and the remainder is absorbed by the cupel. The gold and silver are then parted by treatment with nitric or sulfuric acid ("quartation"). The silver is dissolved but the gold remains unattacked. The brownish residue is then fused and cast into the familiar gold bars to be seen at assay offices or in the mint.



Fig. 98.

(B) The modern process of refining is by means of electrolysis. The crude gold is made the anode. The electrolyte is gold chloride, the cathode, a sheet of pure gold. The silver deposits as a silver chloride "anode mud."

**Properties.** — Gold is a pure yellow, but its color is modified by alloyed impurities so that gold from different "diggings" can be frequently identified by its color. It is the most malleable and ductile of the metals. It is very soft and hence is seldom used in the pure form, since it is materially hardened by the addition of copper or other metal. The value of the articles made from it depend chiefly on their gold content which is expressed either as "fineness," or in carats. Thus a sample 1000 fine is pure gold. One 900 fine is 90 per cent gold. Twenty-four carat (see p. 321) gold is pure gold; fourteen carat is  $1\frac{1}{2}$  gold. American gold coins are 21.6 carat.

Gold has a melting point of 1064° which is lowered by alloying (see p. 253). Its specific gravity is 19.32 and since this is greater than most metals with which it may be alloyed, sophistication of gold may be detected by specific gravity measurement (see p. 76). Gold may be obtained in finely divided colloidal condition (see p. 373), by precipitation of its chloride by reducing agents, in faintly alkaline solutions. In this condition it is of a ruby-red color. Finely divided gold may also be formed by precipitating gold chloride with a very dilute mixture of stannic and stannous chlorides. This precipitate is known as **Purple of Cassius**. Very thin sheets of gold are purple by transmitted light and molten gold is green.

Gold occludes both hydrogen and oxygen to some extent, and also carbon monoxide. Like silver, gold is not affected by oxygen at any temperature and

hence these were called "noble" metals by the alchemists, in contrast with "base" metals like zinc, iron, and tin, which formed "calces" or oxides when heated. The use of the term has been extended to cover the other metals of like behavior and also to describe the argon family of gases. (See Chapter XV.) These metals are also electro-negative in solutions of their salts and hence high positive electrical potential (see Chapter XXVIII) is an indication of inactivity toward oxygen. (See also passive iron, Chapter XXXV.) Gold shows no amphoteric tendencies and hence is not affected by fused alkalies. It reacts readily with the halides directly to form the trichloride and hence is dissolved by aqua regia. (See p. 287.) Its tendency to form double salts is illustrated by the cyanide process. Its atomic weight is 197.2 as a mean of the results obtained by various methods of determination. Its molecular weight is apparently the same as its atomic weight.

**Uses.** — The properties of gold as just outlined, render it extremely useful, not only as a standard value as a medium of exchange, but in many other ways. Gold coin is called "sterling" when it conforms to the specifications of the British mint and contains 91.66 per cent gold, or is 22 carat. This was until 1915 practically the world's measure of value, but under the strain of the great war the standard value became the American dollar, which is 21.6 carat or 90 per cent gold. In the preparation of utensils such as "plate," or tableware, gold alloys as low as 9 carat may be used. In the manufacture of jewelry the standard alloys are 18 and 14 carat. Gold is very extensively used to plate cheap jewelry and preserve fine instruments from corrosion. It is also used for "toning" in photographic processes. For all these manifold uses and also to serve in national gold reserves as a basis for paper currency the supply may be considered limited. The world's production in 1914 was about 680 tons. The chief sources of supply are the United States of America, including Alaska, and the United States of South Africa.

**Compounds.** — There are three chlorine compounds containing gold: auric chloride,  $\text{AuCl}_3$ , chlorauric acid,  $\text{HAuCl}_4$ , and aurous chloride,  $\text{AuCl}$ . The chlorauric acid crystallizes in yellow deliquescent crystals, from aqua regia solutions, with four molecules of water. It is the sodium salt of this acid,  $\text{NaAuCl}_4$ , which is used in photography in "toning" solutions. If the acid is heated gently red auric chloride is formed. The salt is readily hydrolyzed by water to form complex crystals of oxychloride. By heating to  $180^\circ$  the aurous chloride, white and insoluble in water, is formed. It is decomposed by water, gold and auric chloride being formed. By heating the chloride to higher temperature gold is formed. The use of bichloride of gold in the widely-advertised cure for dipomania seems to have been fictitious, though there is apparently a gold salt of chlorauric acid,  $\text{AuAuCl}_4$  or  $\text{AuCl}_3$ .

**Other Compounds.** — When auric chloride is treated with caustic soda, an hydroxide,  $\text{Au}(\text{OH})_3$ , is formed. It is weakly acid in character.



excess of base dissolves to form the salt of the meta-acid  $\text{KAuO}_2$ . There are two unstable oxides,  $\text{Au}_2\text{O}_3$  and  $\text{Au}_2\text{O}$ . Gold salt solutions when treated with ammonia, precipitate "fulminating gold," probably  $\text{AuN}_2\text{H}_3 \cdot 3\text{H}_2\text{O}$ . The double cyanides of gold are produced when gold is treated with an excess of potassium cyanide, e.g.,  $\text{KAu}(\text{CN})_4$ . This is the compound usually employed for electroplating with gold. There are apparently two sulfides of gold,  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_2$ , both somewhat soluble in ammonium sulfide.

**General Properties of Sub-group B.**—The relationship between the elements may be summarized by means of a table as follows:

	Copper, Cu.	Silver, Ag.	Gold, Au.
Atomic weight.....	63.6	107.88	197.2
Specific gravity.....	8.93	10.51	19.27
Atomic volume.....	7.07	10.51	10.11
Melting point.....	1082.6°	960.0°	1062.4°
Conductivity at 0° for 1 cc. in reciprocal ohms.....	$63.4 \times 10^4$	$66.4 \times 10^4$	$44.5 \times 10^4$
Tensile strength per sq. mm. in kilograms.....	10,000–13,000	6000–8000	7000–9000
Valence.....	I and II	I	I and III
Solubility of chlorides, grams per 100 cc. solution	$\text{CuCl}$ 1.5 at 25° $\text{CuCl}_2$ 41.4 at 0° $\text{Cu}_2\text{S}$ $4.94 \times 10^{-3}$ at 18°	$\text{AgCl}$ $1.8 \times 10^{-4}$ at 25° $1.37 \times 10^{-7}$ at 18°	Very soluble
Solubility of sulfide.....	$\text{CuS}$ $3.36 \times 10^{-8}$ at 18°		

**Analytical Relations.**—The three metals do not form an analytical group since silver forms a chloride which is so insoluble that for practical purposes it is completely precipitated with Group I (p. 396). The sulfide of copper is insoluble in dilute acids and therefore appears in Group II. This is also true of the sulfide of gold though the latter, because of its amphoteric nature, is soluble in ammonium sulfide solutions. Gold is, however, seldom sought by wet methods since in the traces in which it is ordinarily found it is more readily collected by the methods of fire assaying (*q.v.*).

**Exercises.**—1. Make a list of the properties of silver, copper and gold which relate them to the alkali metals, and also of those properties which are not presented by the alkalies.

2. How much copper per hour is deposited from a solution of copper sulfate where the cathode surface is 100 sq. cm. and the current density per sq. cm. is 100 milliamperes? How much if the cuprous ion were to be deposited under the same conditions?

3. Write structural formulæ representing basic carbonates, nitrates and acetates of copper. The structural formula of Rochelle salts is  $\text{K}^+\text{OOC}-\text{CHOH}-\text{CHOH}-\text{COO}^-\text{Na}^+$ . Write the probable formula of the copper salt in Fehling's solution (p. 429).

4. Write the equations for the reactions between potassium cyanide and (a) copper sulfate, (b) silver nitrate, (c) gold chloride, showing the formation of the double salts.

5. Why are the sulfates of copper and silver and the chloride of gold acid in solution?

6. Copper and silver dissolve in nitric acid but not in hydrochloric acid. Explain by means of equations.

7. Why will silver chloride dissolve in a solution of ferric chloride?

8. When hydrogen is passed over hot copper oxide what happens? How may this be used to determine the atomic weight of copper? What is needed to give assurance that the value obtained is the true atomic weight?

9. If you were presented with a silver copper alloy and requested to prepare a solution of pure copper sulfate, what would be your procedure?

10. What are the products of reaction between copper and concentrated sulfuric acid? Why is hydrogen not produced?

11. What reactions occur when ammonium hydroxide is added to copper sulfate? Formulate them.

12. If a mixture of copper and cupric oxide weighing 5 grams is heated in a stream of hydrogen until it is completely reduced to copper and the residue weighs 4.5 grams, what percentage of the original material is copper?



## CHAPTER XXV

### ACTINO-CHEMISTRY

IN preceding chapters we have encountered numerous instances where light is produced by chemical action (*vide* pp. 36, 297, 350, etc.). We have also encountered numerous instances of chemical changes produced by light (*vide* pp. 119, 332). It is now necessary to summarize these relations and present some of the more important applications. It is necessary also to present some general ideas concerning light energy. This is essentially a topic belonging to pure physics, so that an outline only will be presented and for details the student is referred to text-books dealing with physics.

**Radiant Energy.** — There appears to exist a form of energy, radiant energy, which travels through empty space with a velocity of 300,000 kilometers per second. Whatever may ultimately be concluded as to the nature of this energy (*vide* electron theory), the conventional view is that it is propagated by transverse waves through "empty" space. (This being difficult to conceive, physicists have imagined an all-pervading substance, "ether," by means of which it is imagined this form of energy is transported.) In terms of the ether hypothesis radiant energy appears to be of varying wave lengths which are capable of experimental measurement, and which vary from 0.1 micron to a maximum as yet not determined. (A micron = 0.001 of a millimeter. Frequently wave lengths are expressed in "Ångström" units where  $10000 \text{ Å} = 1000 \mu\mu$  (millimicrons) =  $1 \mu$  (micron) = 0.001 mm.) Wave lengths from  $0.4 \mu$  to  $0.76 \mu$  are capable of affecting the ordinary eye and producing the sensation of light. Wave lengths greater than  $0.76 \mu$  and less than  $300 \mu$  are known as heat waves and waves from  $2000 \mu$  and upwards (wireless waves) are called electricity. White light appears to consist of wave lengths of great variety and when these strike a material surface they may be either reflected, wholly or partially, or converted into heat, wholly or partially, or they may pass through the matter, which then is said to be transparent (or at least translucent).

**The Spectrum.**—When light enters a transparent medium it is deflected from the straight line of its ordinary progression to a degree which depends upon: first, the angle of incidence of the light; second, the character of the medium; and, third, upon the wave length of the incident light. Other factors being the same, the longer the wave of light the less is its course deflected and consequently when white light is allowed to pass

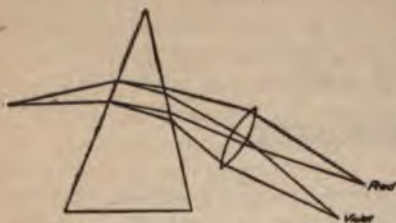


FIG. 99.

through a glass prism (see Fig. 99), it is "dispersed" into a band of light which varies in color from red through orange, yellow, green, blue, indigo, to violet. This band of colored light is known as a spectrum and may be secured by other means than a prism, *e.g.*, the Rowland grating and the Echelon device of Michelson (consult physics texts). By means of instruments more sensitive than the eye it has been shown that sunlight consists not only of light waves proper but of shorter waves ( $0.1$  to  $0.4 \mu$ ) known as the "ultra violet" portion of the spectrum, and also of longer waves ( $0.76$  to  $30 \mu$ ) known as the "infra red" portion. Any instrument by means of which this spectrum may be examined is called a spectro-scope. While Isaac Newton (1675) demonstrated the formation of the spectrum when white light is passed through a prism, it was not until 1860 that Kirchhoff and Bunsen devised an instrument which proved of service to the chemist (see Fig. 100). Since 1860 many varieties of instruments have been devised and the study of various kinds of spectra has revealed to physicists, astronomers, and chemists much of interest and value. Some of these applications will be discussed in subsequent paragraphs.

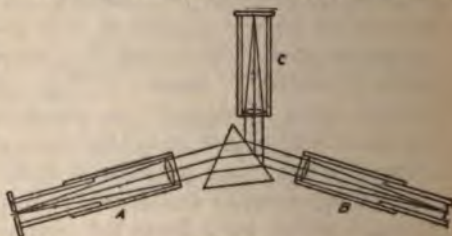


FIG. 100.

**Temperature and Light.**—When any opaque solid or liquid is heated sufficiently it begins to emit light waves. Below  $524^{\circ}$  C. the waves are either too long or are of insufficient intensity to affect



the consciousness. At about 525 degrees the normal eye just begins to get the sensation of light (the **threshold** temperature). The greater portion of the waves are "red" waves and we describe the body as at a "dull red" heat. As the temperature increases the number of shorter waves increases and the color of the object changes through dark red (700 degrees), cherry red (800-900 degrees), bright cherry red (1000 degrees), dark yellow (1100 degrees), bright yellow (1200 degrees), white hot (1300 degrees), blue white (1400 degrees). The light produced is but a fraction of the energy involved and is to be considered but a by-product, the efficiency ranging from 0.05 per cent in the kerosene lamp to 7.2 per cent in the yellow arc light. It is 68 per cent for the mercury arc.

**Bright Line Spectra.** — Objects at white heat or above when examined by means of a spectroscope show a continuous band of light, the complete spectrum. When the substance becomes gaseous, or when gases are heated, the spectra produced are not continuous but consist of a greater or lesser number of separate bright lines (bright line spectra). The color of the gas will then be the resultant of the various wave lengths. Many solid and liquid substances will volatilize at the temperature of the Bunsen flame and hence produce flames colored according to what elements are present (*vide*, alkali metals and alkaline earth metals). These colors are frequently characteristic, *i.e.*, may be used to determine the presence of certain elements. When substances are not readily volatilized by the temperature of the flame, bright line spectra can be obtained by "sparking" the material between suitable electrodes and examining the spectrum so produced. By means of their spectroscope Kirchhoff and Bunsen not only demonstrated that each element in the gaseous state furnishes its own characteristic spectrum, but by superimposing a scale upon their spectra showed the relative position of the lines for many of the then known elements. Bunsen also immediately used the instrument to detect the new elements rubidium and caesium (Chapter XXIII). Since 1861 the spectroscope has been used to discover a number of elements (see thallium, gallium,

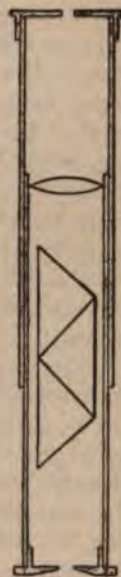


FIG. 101.

indium). It is frequently used to determine the presence of given elements in mixtures and whether a given substance is really new or not (see argon, helium, etc.). The spectroscope is therefore an efficient aid in analysis, and for the detection of small quantities of the more readily volatilized elements small and inexpensive direct vision spectroscopes are available (see Fig. 101).

**Dark Line Spectra.**— Even more fruitful than the constant bright spectra of elements was the further demonstration of Kirchhoff and Bunsen that when white light passes through the vapor of an element a dark line appears in the spectrum where the vapor of the element if itself incandescent would produce a bright line. This phenomenon had been observed in 1802 by Wollaston and in 1814 by Fraunhofer when they found the solar spectrum was crossed by numerous dark lines (Fraunhofer's lines). When these dark lines had been mapped and their positions compared with the bright lines produced by the incandescent gaseous elements in the laboratory it became possible to conclude that in the atmosphere of the sun, as well as in that of other fixed stars, many of the same elements exist which are found in the earth. In one case, that of helium, its existence in the solar spectrum (Janssen, 1868) was observed many years before its discovery on the earth (1898). This use of the spectroscope, with modifications which enable astronomers to estimate the temperature of the stars and to determine whether a star is moving toward or away from the observer have made the development of astronomy particularly rapid in the last three-quarters of a century.

The use of the spectroscope is further increased by the fact that characteristic dark bands are also produced when certain liquids, or solutions, are placed between a source of white light and a spectroscope. For example, a solution of potassium permanganate absorbs the middle portion of the spectrum. Blood also has a characteristic spectrum and the presence of certain substances, notably carbon monoxide, alters it considerably. The use of the spectroscope in these and other ways is called spectroscopic analysis and is of growing importance. A chart of the spectra produced by a few substances is shown in Fig. 102.

**Light by Chemical Action.**— In the preceding discussion the light effects considered are produced by heating substances or



during chemical reactions of the exothermic type; therefore it is difficult to assert positively that the light, which so frequently accompanies chemical reactions, is or is not wholly of secondary origin. In certain cases, however, we have light produced incident upon chemical change where little or no rise of temperature is observed, and where it is certainly below the "threshold" limit of  $525^{\circ}$ .

Cold light may be produced in the laboratory. Ångström got 95 per cent efficiency by passing an electric current through nitrogen at 0.1 mm. pressure. (For the theory of cold light see Bancroft, *Sci. Am. Sup.*, Vol. 80, p. 126.) Examples are furnished by the "cold light" produced by the slow oxidation of phosphorus and of other phosphorescent bodies, as discussed on p. 297. In these cases it is difficult to avoid the conclusion that we have to do with the direct conversion of chemical energy to light, and since in thermoluminescence there is a very small fraction of the total energy lost by the radiating body utilized as light, it would be a very great gain if "cold light" could be directly produced. No successful results have as yet been attained, though the topic is being zealously studied.

There are three other types of light production of special chemical interest. One is known as "triboluminescence," which term is used to describe the light produced when certain substances are disturbed by frictional methods, but scarcely violently enough to produce thermoluminescence. Thus when crystals of uranium nitrate, sugar and many other substances are crushed, light is produced. Again, many substances when crystallized in the dark produce flashes of light, not very intense but distinctly visible. Again, mention was made on p. 297 of substances which give off light for a period after having been subjected to the action of intense light. This is called phosphorescence, but is clearly not to be ascribed to the same cause as that of decaying wood or animal phosphorescence. It is a property possessed by comparatively few substances at ordinary temperature but by most substances at very low temperatures. It is this property which gives to mixtures of certain sulfides their use as luminous paints. This behavior is doubtless closely related to the production of light when X-rays or the rays from radium fall upon certain substances such as zinc sulfide, calcium fluoride, diamonds, barium platinocyanide and many other substances. This last mode of behavior is called fluorescence and may or may not be analogous

the behavior of certain liquids such as kerosene and other mineral oils, solutions of quinine, etc., which "fluoresce" in the sunlight. These light phenomena are not readily explained in a wholly satisfactory manner.

**Absorption of Light During Chemical Change.** — When light acts on chemical substances it may cause either a rise in temperature or cause direct conversion of light energy into chemical energy. The latter is of course the only real photochemical action, but it is sometimes difficult to properly assign the proportions of the results produced.

By far the most important of all such effects is that of light upon plant growth (p. 332). When carbon dioxide and water are brought together the only chemical reaction taking place at ordinary temperatures is the formation of a small percentage of carbonic acid. When, however, a reaction takes place in plant cells under the influence of sunlight in the presence of chlorophyll the reaction which takes place probably is  $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{CH}_2\text{O}$ . The formaldehyde so produced is further metamorphosed in plant processes to produce various carbohydrates and their derivatives. This process takes place only within certain ranges of temperature, and sunlight operates not only as the means of producing the favorable temperature, but also otherwise, since plant growth will not take place continuously, in the dark. Only a very small portion of the energy reaching the earth is utilized in this manner. It is estimated by Le Chatelier that 2,100,000 greater calories per square meter per year reach the earth and the quantity of carbon in the plant growth per year is, under favorable conditions, not above 100 grams, which corresponds to about 800 greater calories, or less than 0.04 per cent of the energy received. This fraction, small as it is, serves for the maintenance of all animal activity on the earth, together with a large margin for posterity (see Fossil Fuels — Geological Texts), and for the waste of decay. It is a fascinating problem to seek both to increase the percentage of sunlight used and to decrease the waste of that already stored up. These are the great problems of agriculture and conservation.

Photochemical absorption is by no means limited to plant growth. Literally hundreds of reactions have their course determined or their rate influenced by sunlight, and it is probable that the known list would be vastly increased were more reactions studied in the dark. Examples of reactions produced by light



80 75 70 65 60 55 50 45 40



FIG. 102.

FIG. 102.

12

12



or modified by light are: The change of yellow to red phosphorus (see p. 299); the union of hydrogen and chlorine (p. 123); the decomposition of silver nitrate (p. 435); phosgene (p. 119). Very many organic reactions are influenced by light. The light most effective in the production of such chemical changes is that which lies beyond the violet end of the spectrum, with wave lengths less than visible rays, and certain sources of light consist either largely or wholly of such radiations. Examples are furnished by the arc of incandescent mercury (the mercury lamp), the flame of burning magnesium, the Roentgen Rays (X-Rays), the radiation from radium (*q.v.*), etc. These are then usable for the purpose of producing such changes.

**Photography.**—The most extensively utilized photochemical effects are those which serve to make permanent images. These processes are collectively known as photography, and depend on a number of physical and chemical relations only a portion of which have to do with light. The art is highly developed and in many cases has outstripped the ability of science to give satisfactory explanation. A full discussion of the subject is out of place here and the attempt will only be made to outline the representative steps.

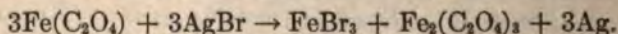
**The Negative.**—When silver chloride is exposed to the sunlight it changes in color from white to violet and ultimately to black. This change of color is accompanied by evolution of chlorine and the colored mass is apparently a mixture of metallic

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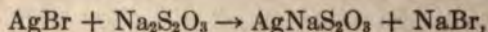
silver and silver chloride,  $x\text{AgCl} \rightarrow y\text{Ag} + w\text{AgCl} + z\text{Cl}_2$ . This reaction is facilitated by substances which absorb the chlorine, *i.e.*, by reducing agents (Chapter VII). This is illustrated by the behavior of silver nitrate, which remains unchanged, at least visibly, in the sunlight when dry, but when moist and in the presence of reducing agents is reduced to metallic silver. Furthermore, a salt in which such decomposition is initiated by light is more rapidly reduced by reducing agents than that not so affected. These are the facts utilized in the preparation of photographic negatives. A "plate" or "film" is prepared\* by making an emulsion of silver nitrate and gelatine. To this emulsion is added ammonium bromide. The reaction,  $\text{AgNO}_3 + \text{NH}_4\text{Br} \rightarrow \text{AgBr}$

\* For "Evolution of the Dry Plate," see *Sci. Am. Sup.*, Vol. 20, p. 126.

+  $\text{NH}_4\text{NO}_3$ , produces a very fine-grained deposit of silver bromide, which is more sensitive to light than is silver chloride. After washing out the ammonium nitrate the gelatine is dried either on glass plates, or on thin collodion films, or even alone. Before drying these films are allowed to stand, or "ripen," until the silver bromide has collected into somewhat larger particles than are at first formed. These larger particles are more readily affected by light. The plates are also "sensitized" by exposure to iodine vapors. When the plates are prepared they are "exposed" for a very brief time to the action of light in a camera. The function of the camera is to focus upon the plate the image of some object. The effect of the light is to initiate the change  $\text{AgBr} \rightleftharpoons \text{Ag} + \text{Br}$ , and the effect is proportional to the intensity of the light and the time of exposure. After exposure, though no visible effect is produced, the plates will continue to undergo the above change if placed in reducing solutions, the more intensely illuminated portions being more rapidly reduced. By watching the process carefully a point of maximum definition of the image can be seen by the relative quantities of silver deposited on the film. (The silver, being finely divided, is black in color.) When this point of definition is reached the development is stopped by removing the developer and dissolving any undecomposed silver bromide by means of a suitable solvent. The "negative" then shows an image of the object photographed, in which the lighter portions of the object are darker in the negative. The developers most extensively used are organic compounds readily oxidized such as pyrogalllic acid, hydroquinone, etc. (see Organic Chemistry). The solvent used for the unchanged silver salts is almost exclusively the sodium thiosulfate (hypo). An example of the reactions involved in development may be given as follows: Ferrous oxalate,  $\text{Fe}(\text{C}_2\text{O}_4)$ , will readily be converted into compounds in which the iron is trivalent. With silver bromide we have



The reaction with the thiosulphate may be represented by the equation:

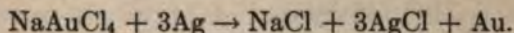


both products of the reaction being soluble (see also p. 434).

**Printing.**—In printing from negatives the process is similar to that already outlined. The negative is placed over a film,



or paper, sensitized by silver salts, and exposed to light. The darker parts of the negative protect the sensitive layer beneath from the action of light in proportion to their density. When the new film is developed the original light shades are obtained. In printing, the same sensitive film as used in the negative is employed, or, since time is usually not limited, as in the photographing of a live object, a less sensitive material, such as silver chloride, may be used and the required amount of silver may be deposited by action of light alone. The fixing of the image is carried out as before. The silver print is not very stable and may be made more permanent, *i.e.*, less affected by the atmosphere, by plating it with gold or platinum. This operation is called "toning." This reaction may be indicated:



The film of gold not only makes the print more durable but adds to its beauty.

The number of materials used for the printing end of photographic processes is very great and the "processes" patented, secret and otherwise, are beyond the scope of our present purposes. It should also be emphasized that the above discussion is only a very meager outline of the subject. For details of processes, methods, reactions, developers used, toning reagents, color photography, etc., the student is referred to Sheppard's Photochemistry. An excellent historical sketch is found in A. Broth's Manual of Photography.

## CHAPTER XXVI

### GROUP II—SUB-GROUP A

GROUP II of the periodic system consists of two fairly well defined sub-groups, sub-group A being made up of the elements calcium, strontium, barium and radium, while sub-group B consists of magnesium, zinc, cadmium and mercury. The type member of the group, beryllium, like all the members of the first series, shows fairly marked divergence of properties from both sub-groups. It will be discussed in connection with sub-group B. As in group I the fullest discussion will be given the more important elements and less full discussion of the others.

#### CALCIUM

**Occurrence.**— Calcium is fifth among the elements in the order of quantity found in the lithosphere (p. 5). It does not occur free as is to be expected from its properties (*vide infra*). Its compounds are very widespread as well as abundant. The variety of its natural forms is also unusually great. The **carbonate**,  $\text{CaCO}_3$ , occurs in various forms as calcite, varieties of which are Iceland spar, dog-tooth spar, and satin spar, all of which are crystalline substances of definite forms; marble, which consists of crystalline grains closely compacted in more or less fine-grained masses; limestone, which is a dull compact mass of non-crystalline character; chalk, a soft white material; calcareous marl, soft and mixed with clay. Besides these varieties there are many of less important though still abundant forms, such as onyx, which is a variety formed by deposition from water and shows streaks and layers of other material; stalactites and stalagmites, cavern deposits; lithographic limestone; hydraulic limestone, etc. There are also enormous masses of dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , which is also called mountain limestone. The carbonate also is found in solution in many water supplies as the acid carbonate,  $\text{Ca}(\text{HCO}_3)_2$ . The **sulfate** is also abundant, being found as anhydrite,  $\text{CaSO}_4$ , in rock salt deposits and elsewhere, and as gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , of which there are



two chief varieties, alabaster and selenite. The sulfate, being somewhat soluble in water, is frequently found in surface waters (*vide infra*). The **phosphate** also occurs in great masses and chiefly in two forms, apatite,  $\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$ , and phosphate rock, or phosphorite, which is the more or less pure phosphate. The **fluoride**,  $\text{CaF}_2$ , is also an abundant mineral. It is known as fluorite, also as fluorspar. **Calcium tungstate**,  $\text{CaWO}_4$ , known as scheelite, is the most abundant source of the rare metal tungsten (*q.v.*). The **chloride**,  $\text{CaCl}_2$ , is found in many surface waters and as tachydrate,  $\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , in salt deposits. Besides these mineral forms calcium is found either as the chief metal or as a replacing metal in a great variety of **silicates** (*vide pp.* 369–370). Calcium compounds are also found in a great variety of plants and hence some form of calcium salt is essential to soil fertility. Calcium phosphate is the chief mineral constituent of the bones of animals and the carbonate is the most important constituent of the shells of many animals, and of the shells of eggs.

**History.** — The name **calcium** is derived from the latin “calx” or lime and the use of the latter as mortar in ancient structures indicates its great antiquity as a building material and of the knowledge of the calcining of lime, but it was not until 1755 that Black (see *Alembic Club Reprints*, No. 1) showed the relation between quicklime ( $\text{CaO}$ ) and the carbonate. In 1808, Davy made impure calcium and in 1898 Moissan made pure calcium by reduction of the oxide by sodium.

**Preparation.** — Calcium is prepared at present by electrolysis of the fused chloride. The anode is a graphite crucible and the cathode an iron rod. The temperature of the bath is regulated so that the metallic calcium adheres in the solid form to the rod and the latter is withdrawn as fast as the formation of metal permits, and thus a cylinder of

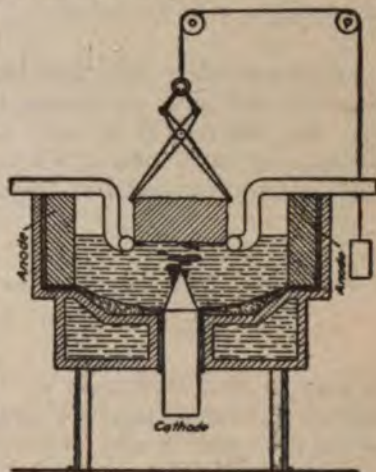


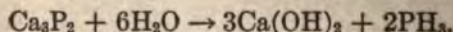
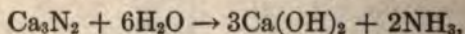
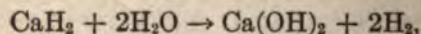
FIG. 103.

the metal finally serves as the anode. This method was devised in 1908 by Seward Von Kugelgen (see Fig. 103), and renders the production of calcium fully as cheap as that of sodium.

**Properties.** — The metal is a silver white lustrous metal. Its specific gravity is 1.52. It tarnishes readily in the air and decomposes water at the ordinary temperature, liberating hydrogen. It also reacts with acids vigorously. It burns readily in air, forming the oxide. It also combines directly at high temperature with nitrogen and forms the nitride,  $\text{Ca}_3\text{N}_2$ . It unites readily also with halogens, with sulfur, silicon, phosphorus, etc.

**Uses.** — The element, only recently obtainable at reasonable cost, finds but little practical application as yet. It may be used to create a very high vacuum in sealed tubes, since by heating it unites with both nitrogen and oxygen. It may in the future find more extensive uses since its properties are such as to recommend it for a variety of purposes at present otherwise served. On the other hand, its compounds, both natural and artificial, find a huge variety of uses, but they may for the most part be prepared without starting with the metal.

**Compounds.** — The hydride, nitride, and phosphide may all be readily prepared by heating the metal with the proper element, but the last-named is more conveniently prepared by passing phosphorus vapor over red hot lime. These compounds all react with water as indicated by the equations:



It may be that eventually calcium hydride will be the most convenient laboratory means of preparing small amounts of hydrogen as the phosphide is now for preparing phosphine.

**Calcium Halides.** — Calcium fluoride,  $\text{CaF}_2$ , fluorspar, is mined in large quantities and serves as a flux in various metallurgical operations, where its function is to lower the temperature at which the slags melt. It is this application which gives it the name (*fluor* = a flow and *spar* = a mineral). It is used also in the



preparation of certain varieties of opaque glass and enamels. It is the chief source of fluorine compounds and particularly of hydrofluoric acid. It becomes luminous when heated, long before the "threshold" temperature is reached thus giving rise to the term "fluorescence" (Chapter XXV). The salt is nearly insoluble in water and hence is produced when soluble fluorides are added to solutions of calcium salts. This behavior is very remarkable in view of the very great solubility of the other halides, but we must recognize that fluorides do not "play the game according to the rules," as witness also the solubility of silver fluoride while the chloride is insoluble. We can associate these peculiarities in our minds with the double molecule of hydrofluoric acid,  $\text{H}_2\text{F}_2$ , though whether there is real connection or not does not appear certain.

Calcium chloride,  $\text{CaCl}_2$ , is a by-product in many manufacturing processes (see p. 406) and since it finds no very large technical applications it is very cheap. By evaporating its solutions in water large six-sided prisms of the hexahydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , are formed. These crystals are very deliquescent. They dissolve in water with lowering of the temperature, and with ice form a eutectic mixture, only at a temperature of  $-55^\circ$  (*vide* p. 257).

Besides the hexahydrate, an examination of the solubility curve in the light of the phase rule (*q.v.*) reveals the existence of a mono-, a di-, and two tetra-hydrates (Fig. 104). When we drive off the water from these hydrates by evaporation some hydrolysis occurs (*cf.*  $\text{MgCl}_2$ ) and the residue contains some oxide. When, however, the hexahydrate is heated to  $200^\circ$  it still retains two molecules of "water of crystallization" and forms a porous white mass of very low

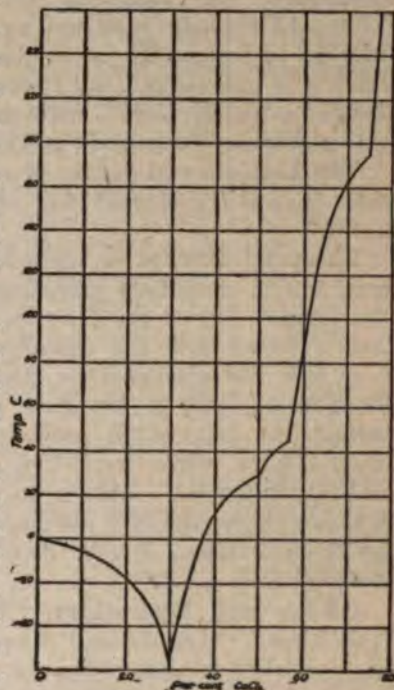


FIG. 104.

vapor tension and hence is very convenient as a drying agent for gases. It is extensively used for this purpose under the name "granulated calcium chloride." All hydrates have a certain vapor tension and consequently even calcium chloride cannot extract all the moisture from a gas. The most effective agent for this purpose is phosphorus pentoxide, because its "hydrate," metaphosphoric acid,  $\text{HPO}_3$ , has no measurable vapor tension. Moreover, calcium chloride forms analogous compounds with ammonia, *e.g.*,  $\text{CaCl}_2 \cdot 6\text{NH}_3$ , and hence the granulated chloride may not be used for drying this gas. The chloride is frequently used also for drying organic liquids in which it is not soluble, but it should be remembered that alcohols also form "alcoholates" with calcium chloride,  $\text{CaCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$  (*vide* molecular compounds, p. 417).

The bromide and iodide of calcium are even more soluble in water than is the chloride, but otherwise offer no points of special interest.

**Bleaching Powder** is manufactured by passing chlorine into large leaden chambers containing slaked lime spread out into thin layers. When the lime is "saturated" with chlorine, lime dust is blown into the chamber to absorb the excess chlorine. It is also manufactured by passing mechanical conveyers in a direction contrary to the flow of a stream of chlorine. In this method the chlorinated product comes out of the chamber in finished form, while fresh hydroxide encounters the gas at its least concentration. This is an admirable illustration of the law of mass action applied industrially. The product is known as "chloride of lime," which certainly it is not, and as "bleaching powder" (*vide* p. 191).

**Oxides and Hydroxides.**—Calcium oxide,  $\text{CaO}$ , known as "quicklime," "burnt-lime," "caustic lime" or simply "lime," is not found free in nature but may be obtained readily by heating the carbonate. The substance has been used technically since very ancient times and its adaptability to various purposes is such that it is prepared in huge quantities. The devices used for the purpose are known as lime kilns. Formerly limestone was heaped up with alternate layers of fuel and with suitable air passages. The whole heap was then covered with turf and the fuel ignited. When the whole mass was heated thoroughly the air holes and vents were closed and the mass allowed to cool out of contact with air. The kiln was then opened and the mass



sorted into various grades of lime, according to degree of whiteness and burning. This method has been almost entirely supplanted by the continuous kiln (Fig. 105) into which the raw limestone may be fed and the finished lime withdrawn without interruption of the process. This process has been very carefully studied. It is a reversible reaction and if the limestone is heated in a closed vessel an equilibrium results,  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ , with a definite gaseous pressure corresponding to each temperature. The following data show the values of this pressure at the corresponding temperature (Jour. Amer. Chem. Soc. 32,938.)

Temperature.....	587°	680°	743°	800°	852°	894°
Pressure in mm. of mercury...	1.0	15.8	60	183	381	716

It will be apparent then that so long as the limestone has a dissociation pressure greater than the partial pressure of the carbon dioxide above it, it will continue to dissociate. This relation is analogous to the behavior of liquids, of hydrates, etc., and according to the phase rule (Chap. XIII) is a univariant system in which neither temperature nor pressure can be altered without altering the point of equilibrium. We have then  $P (= 3) + F (= 1) = \text{components} + 2$ . The number of components is apparently three,  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{CO}_2$ , but it must be observed that only two are independently variable, since for every molecule of calcium oxide produced one of carbonate is destroyed (*cf.* definition of component, Chap. XIII). The system,  $2\text{BaO}_2 \rightleftharpoons 2\text{BaO} + \text{O}_2$ , is a similar univariant system. (See p. 30.)



Fig. 105.

It follows from the above considerations that the burning of lime proceeds more rapidly by keeping the carbon dioxide pressure low. This is accomplished by free passage of air through the kiln. The product of the limekiln is a more or less pure product according to the purity of the limestone "burned." If impure limestone is used it is burned at as low a temperature as possible, since otherwise the lime fuses with the clay present and forms insoluble granules which interfere with the subsequent utilization of the lime. Lime made from pure limestone is frequently called "fat lime."

Pure calcium oxide is a white porous solid with a specific gravity

of 3.3. When heated in the oxyhydrogen flame it glows with an intense white light (the limelight). It can be melted at  $1900^{\circ}$  and in the electric furnace (temperature about  $3500^{\circ}$ ) it boils and the vapor condenses in the form of crystals. Calcium oxide cannot be reduced by carbon to the metallic form since at the temperature required for reduction it unites with carbon to form the carbide (*q.v.*). When lime is treated with water an exothermic reversible reaction takes place,  $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2 + 15,500 \text{ cal.}$ , and if but a small excess of water is added it may be heated to boiling. This process is called "slaking" of lime. This reaction takes place with water vapor and hence lime may be used for drying gases, particularly for ammonia (*cf.* p. 454). Also as a consequence lime "air slakes," and from the hydroxide gradually reverts to the carbonate, when exposed to the air.

The uses of the oxide are for the most part dependent upon the preliminary conversion to the hydroxide. This conversion may either be carried out as the utilization of the hydroxide takes place, as in the preparation of mortar, or it may be done as an independent operation and the hydroxide marketed. Lime is used as such in many operations, as the manufacture of cement and of carbide, but in such cases is ordinarily prepared as used.

**Calcium Peroxide**,  $\text{CaO}_2$ , can be made by treatment of the hydroxide with hydrogen peroxide and subsequent dehydration at  $130^{\circ}$ . It is not made by direct heating of the oxide, as is the case with the peroxides of sodium and barium.

**Calcium Hydroxide** is but slightly soluble in water, 1.76 g. per liter at  $0^{\circ}$ , and its solubility decreases with rise of temperature, being 0.77 g. at  $100^{\circ}$ . Its solution is strongly basic, considering the concentration, and is known as lime water, and is extensively used in medicine, as an "antacid." Because of its low cost, calcium hydroxide is used very extensively, either dry, as in the manufacture of bleaching powder, or as a suspension in water, milk of lime, or as a paste (the "putty" of the plasterer).

To describe the modes of use of the hydroxide in its various applications would take too much space and the interested reader is referred to a special article in *The Mineral Resources of the United States*, Vol. II, 1915. The following partial list will indicate the scope of its industrial uses: In the manufacture of sand lime brick, glass, ceramics, soda ash and caustic soda, bleaching powder, calcium carbide, calcium cyanamide, fruit and tree sprays, sugar



paper, paints, glycerine, lubricants, candles, tannin, glue, varnish, white wash, etc., etc.

One most important utilization of slaked lime should be discussed. When it is mixed with sand and water in proper proportions a thick plastic mass, known as **mortar**, is produced. This may be used to fill in the crevices between building stone or brick and by its "setting" serve as a binder between the separate fragments. The mortar first loses the admixed water, by evaporation, and forms a porous mass, and gradually the carbon dioxide of the air converts the hydroxide to the carbonate. If mortar is made with an admixture of hair or other fibrous material it is sufficiently coherent to be used as "plaster" and was, and still is, used in large volume for this purpose. Of recent years a "wood pulp plaster" is to a large extent replacing it. (See plaster of Paris.) Some idea of the value of lime and its hydroxide may be gained if we consider that its annual production in the United States is about 4,000,000 tons.

**Calcium Carbonate,  $\text{CaCO}_3$ , and Bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$ .** — The various deposits of calcium carbonate which are found in nature are of four general types; crystallized, as calcite and aragonite, two forms which are related to each other as are rhombic and monoclinic sulfur. The calcite, in several types of crystals, is hexagonal, has a specific gravity of 2.70 to 2.75, and is the stable form. The rhombic form with a specific gravity of 2.92 to 3.28 changes rapidly at  $500^\circ$  to the hexagonal form. Marble and limestone are massive and the former consists of distinctly crystalline minute particles, probably formed by slow metamorphosis of deposits of limestone. The latter is found in all degrees of transition from the amorphous form to the clearly crystalline type. Chalk, coral, etc., are made up of the shells or other structures of marine animals. Other samples of organic origin are eggshells and pearls. The fourth type is the highly impure samples of carbonate associated with other mineral forms such as dolomite and marl (*cf.* occurrence of calcium). The purest forms of carbonate are crystals known as Iceland spar, which is frequently used in standardizing solutions (see quantitative texts). Calcium carbonate is very insoluble in water ( $1.3 \times 10^{-3}$  g. in 100 cc. of solution at  $16^\circ \text{C.}$ ), and is precipitated from soluble calcium salts by addition of soluble carbonates (see analytical reactions). The solubility of freshly precipitated amorphous carbonate is greater than that of the crystalline variety.





water (solubility 0.17 g. per 100 cc. at 0° and increasing to 0.21 g. at 38° and decreasing again to 0.174 g. at 100°) (see p. 84). When heated to 107° the gypsum loses water and forms a white powder,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , called **plaster of Paris**. The same substance is formed at 150° when water and gypsum are heated under pressure. It is therefore a constituent of "boiler scale." The reaction,  $2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons (\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$ , is slow in the reverse direction at ordinary temperature and hence the plaster of Paris may be mixed with water to form a paste and then molded into desired forms. When this paste is made with about one-fourth water and three-fourths plaster by weight it "sets" to a white porous mass with a slight increase in volume. It is therefore invaluable for making casts, models, and many sorts of decorative work. Mixed with sand it is used to make the "hard finish" of ordinary plaster and with wood fiber it is used at present in vast amounts to form "wood fiber plaster." The time of setting is much delayed by retarding catalyzers such as alum, borax, etc. When gypsum is heated above 125° the anhydrous substance is formed, which sets much more slowly than the hemihydrate. This is called "dead burnt plaster." It is used to make floors. The material known as stucco, used for temporary structures, such as exposition buildings, is a mixture of plaster of Paris and coarse sand (see also Mellor, p. 445). Great quantities of gypsum are used for fertilizer both alone and as a constituent of prepared fertilizers (*q.v.*). It is supposed to function in this relation by double decomposition with ammonium carbonate formed by plant decay,  $(\text{NH}_4)_2\text{CO}_3 + \text{CaSO}_4 \rightarrow \text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ . The ammonium sulfate, being more stable than the carbonate, remains longer in the soil. Sulfuric acid in small amounts has recently been shown to be a stimulant to plant growth and it may be that calcium sulfate by hydrolysis with water furnishes this needed trace of acid.

**Calcium Sulfide.**—When calcium sulfate is heated with carbon it is reduced to the sulfide,  $\text{CaSO}_4 + 4\text{C} \rightarrow \text{CaS} + 4\text{CO}$ . The sulfide is but slightly soluble in water, but is slowly hydrolyzed,  $2\text{CaS} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{Ca}(\text{SH})_2$  and then,  $\text{Ca}(\text{SH})_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + 2\text{H}_2\text{S}$ . These reactions go almost to completion because of the slight solubility of the calcium hydroxide and the weak character and relative insolubility of the hydrogen sulfide. It is because of this hydrolytic action of water that calcium is not precipitated from solutions by soluble sulfides with the third group metals (p. 396). Calcium sulfide is a white substance and,

like certain other sulfides, when exposed to intense light, will appear luminous when placed in the dark. It is the chief basis of luminous paints (Chap. XXV). Apparently luminescence is not a property of the pure sulfide but depends in some obscure way upon traces of other sulfides. Calcium sulfide unites directly with sulfur to form polysulfide,  $\text{CaS}_x$ , which in solution is extensively used as a tree spray. It is made by boiling "milk of lime" with an excess of sulfur. A solution of this at one time had extensive sale as a medicine under the name "Sulphuro" or soluble sulfur. A curious set of reactions were used by the Germans during the great war to secure sulfuric acid. Germany is not rich in sulfides and has no sulfur and due to the blockade could not import any. Therefore they reduced  $\text{CaSO}_4$  to  $\text{CaS}$ , and treated this with hydrochloric acid (obtained from salt by electrolysis) to form  $\text{H}_2\text{S}$ . This being burned furnishes the needed sulfur dioxide to produce sulfuric acid.

**Calcium Phosphate.**—The phosphates of calcium are three in number:

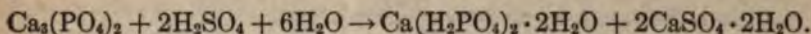
Calcium orthophosphate (tertiary).....	$\text{Ca}_3(\text{PO}_4)_2$
Secondary calcium phosphate.....	$\text{CaHPO}_4$
Primary calcium phosphate.....	$\text{Ca}(\text{H}_2\text{PO}_4)_2$

The first occurs in nature as phosphorite and apatite (the latter usually with  $\text{CaF}_2$  or  $\text{CaCl}_2$ ) and these are the chief sources of both phosphorus and phosphoric acid (*cf.* p. 297 *et seq.*). It is also obtained by ignition of bones and is about 80 per cent of their ash. The ashes of all plants contain phosphates as do all manures (such as barnyard manure, guano, etc.). The orthophosphate is very insoluble in water but is very slightly decomposed by water. It is somewhat more soluble in soil water and hence is available as a plant food. (See fertilizers.) The orthophosphate is soluble in acids and, by appropriate quantities of sulfuric acid, is converted to calcium sulfate and either phosphoric acid or primary or secondary calcium phosphate. The primary phosphate is used as fertilizer and as an acid factor in phosphate baking powders (*cf.* p. 408).

**Fertilizers.**—Since phosphates are essential both as plant food and, through plants, for animal food, and since the amounts present in soils are ordinarily insufficient, either in quantity or in available form, to supply the plant demand under intensive cultivation, huge quantities of phosphates are mined and converted to forms suitable



for fertilizers. Therefore this seems a suitable place to present the general subject of fertilizers which has been frequently referred to in preceding pages. \*When calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is treated with chamber acid (p. 235), the following reaction takes place:



At the same time some secondary salt is formed, so that  $\text{CaHPO}_4$  is also present in the resulting mass, and also some free phosphoric acid and undecomposed tertiary phosphate. The mass on standing "reverts" somewhat and ultimately contains only the primary and secondary phosphates and gypsum. The purpose of this treatment is to obtain as much phosphate as possible in the form of the soluble salt, the "superphosphate,"  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , and as little in the form of the less soluble secondary salt. (The relative solubilities are, at  $30^\circ$ ,  $\text{CaHPO}_4$  0.23 g. per liter of solution and  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  upwards of 18 grams. A much more concentrated solution can be obtained, but it decomposes with gradual deposition of the secondary salt.) The mixture of phosphate and sulfate is placed on the market as such and provides the plant food in readily available form for the growing plants. What is not at once utilized "reverts" with the basic constituents of the soil, *e.g.*,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{CaCO}_3$  (or  $\text{Fe}_2\text{O}_3$ )  $\rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O} + 2\text{CO}_2$ , to form insoluble phosphate which, being in a state of fine division in the soil, is by soil water and plant acids made readily utilizable by plants.

Since plants require not only phosphates but also nitrogen compounds and potassium salts, the usual form of fertilizer is the so-called "complete" or "mixed" fertilizer. This is a mixture of potassium chloride or sulfate and ammonium sulfate or sodium nitrate with the superphosphate. The mixture owes its chief value to the potassium, combined nitrogen and soluble phosphate present and it is usual to compel manufacturers of fertilizer to place analyses upon the sacks showing their content expressed as percentage of potassium oxide, combined nitrogen and "phosphoric acid,"  $\text{P}_2\text{O}_5$ , in the mixture. This type of fertilizer is now being replaced somewhat by cyanamide (*q.v.*). Some phosphate for fertilizer is being obtained now from the "basic slag" of the open hearth furnace (*q.v.*). The quantity of phosphates used as fertilizers is indicated by the fact that upwards of three million tons of calcium phosphate are annually mined in the United States alone. It

comes chiefly from South Carolina, Florida, and Tennessee. There is no danger of exhaustion of the supply for there are enormous deposits of practically untouched phosphate rock in Idaho, Utah, and Wyoming.

**Other Salts of Calcium.** — Many other salts of calcium are of value, but detailed discussion is omitted. Among these are: Calcium acid sulfite,  $\text{Ca}(\text{HSO}_3)_2$ , used on a large scale for the preparation of paper pulp from wood; calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , manufactured on a large scale by the Birkeland-Eyde Process (*q.v.*) at Notodden, Norway; calcium oxalate,  $\text{Ca}(\text{C}_2\text{O}_4)$ , a very insoluble salt used as a means of qualitative detection and quantitative estimation of calcium; calcium acetate,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ , a by-product of wood distillation and used as a source of both acetic acid and of acetone (*q.v.*); calcium silicate,  $\text{CaSiO}_3$ , a factor in nearly all sorts of glass (*q.v.*); calcium carbide (*q.v.*), used as a source of acetylene, (*q.v.*); calcium cyanamide,  $\text{CaCN}_2$ , a fertilizer to which frequent reference has already been made. There are, of course, many other salts of less importance.

#### STRONTIUM AND BARIUM

**Occurrence.** — These elements occur widely distributed through igneous rocks but are much less abundant than calcium. Deposits of the carbonates and sulfates of both are fairly abundant. Strontium carbonate,  $\text{SrCO}_3$ , is known as strontianite, barium carbonate,  $\text{BaCO}_3$ , as witherite, strontium sulfate,  $\text{SrSO}_4$ , as celestite and barium sulfate,  $\text{BaSO}_4$ , as barite or heavy spar.

**History and Preparation.** — Strontium gets its name from Strontian, a village in Scotland near which its carbonate was discovered (1787); barium from barite (from *βάρυς* = heavy) because of the great specific gravity of the natural sulfate. Barium sulfate was recognized as containing a special "earth," or oxide, by Scheele, 1774, and strontianite as containing a special earth by Crawford, 1790. The impure metals were first prepared by Davy, 1807. Both metals can be prepared by the method used for calcium (*q.v.*), but neither is prepared on any large scale.

**Properties.** — Both metals are silver white and soft, both react with water to liberate hydrogen, and when heated with hydrogen form the hydrides. Their properties are otherwise sufficiently detailed at the close of the chapter.

**Compounds.** — The only compounds of strontium deserving special mention are the nitrate,  $\text{Sr}(\text{NO}_3)_2$ , used as a constituent of red fire in pyrotechnics, and the hydroxide,  $\text{Sr}(\text{OH})_2$ , which forms a readily crystallizable compound with sugar,



from which the sugar can be again recovered. It is, therefore, used to some extent to obtain sugar from uncrystallizable syrups. It must be recognized that strontium can form the complete series of salts analogous to those of calcium, but except for differences of a minor sort they offer no special points of interest. (See analytical reactions.) The same statement may be made in general for barium compounds with the exception of the following:

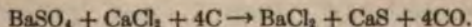
**Barium Oxide.** — The carbonate of barium is much less readily dissociated by heat than is calcium carbonate so that it is not economical to prepare the oxide from witherite directly, but if carbon be heated with the carbonate the carbon dioxide by partial pressure is kept practically at zero by conversion to the monoxide,  $\text{BaCO}_3 \rightleftharpoons \text{BaO} + (\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO})$ , and hence at reasonable temperatures the dissociation is fairly rapid. The oxide is also readily prepared by heating the nitrate. It is more readily soluble in water than is the calcium hydroxide and the hydroxide formed is a strong base. The base may also be prepared by heating the carbonate in superheated steam. This illustrates the effect of decreasing the concentration of both factors of a reversible reaction. Thus, when at a given temperature we should have with small partial pressure of carbon dioxide an equilibrium condition of the reaction  $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$ , the passage of steam over the mass not only keeps the pressure of carbon dioxide low but also converts the oxide to hydroxide.

The hydroxide is used to a very considerable extent as a standard reagent. Its solution is known as "baryta water." The oxide is used most extensively to prepare the peroxide. The dissociation pressure of barium peroxide is  $(2\text{BaO}_2 \rightleftharpoons 2\text{BaO} + \text{O}_2)$ ,

Temperature.....	525°	670°	735°	775°	790°
Pressure in mm.....	20	80	260	510	670

Since the partial pressure of oxygen in the air is about 160 mm. it follows that if air be passed over barium oxide at 670°, or a little above, oxygen will be absorbed and that at increased pressure of air, thus increasing the partial pressure, still higher temperatures may be used to cause the reaction to go  $2\text{BaO} + \text{O}_2 \rightarrow 2\text{BaO}_2$ . On the other hand, if by means of an exhaust pump the partial pressure of oxygen be kept low the reaction will proceed  $2\text{BaO}_2 \rightarrow 2\text{BaO} + \text{O}_2$ . (See p. 30.) It will be obvious from the above discussion that air used for the above purpose must be free from carbon dioxide if the process is to be continuous. The importance of barium dioxide is largely due to its use in the preparation of hydrogen peroxide (*q.v.*).

**Barium Chloride,**  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , is readily formed by treatment of the carbonate with hydrochloric acid or it may be formed by heating the sulfate with calcium chloride and carbon,



The chloride of barium is soluble in water and may be purified by recrystalliza-

tion. It is extensively used as a laboratory reagent in estimation of sulfuric acid and sulfates.

**Barium Sulfate**,  $\text{BaSO}_4$ , is the most abundant natural form of barium and also its most extensively used salt, since it is used as a pigment, "permanent white," as a substitute for white lead (*q.v.*), and also as a starting point for the preparation of other barium compounds. It is one of the most insoluble of sulfates and consequently is precipitated almost completely when sulfates are treated with soluble salts of barium. It is, therefore, frequently employed in analytical operations. Other salts of barium which have more limited uses are the nitrate,  $\text{Ba}(\text{NO}_3)_2$ , and  $\text{Ba}(\text{ClO}_3)_2$ , which are used in pyrotechnics. The chromate,  $\text{BaCrO}_4$ , is used as a means of detection both for chromates and barium salts. The sulfide,  $\text{BaS}$ , is used as a factor of luminous paints.

## RADIUM

**Occurrence and History.** — The last member of sub-group *A* is a very rare element, though it occurs in minute amounts very widely distributed. Because of its very remarkable properties (*vide infra*) it has taken a large hold upon the popular imagination and because of these same properties and deductions from them it is of the very highest scientific importance (Chap. XXXVI). It is, therefore, a very well known element. It was discovered in 1903 by Madame Curie, though the property which has given it its name was discovered in 1896 by Becquerel (see Uranium), and the search for the source of the radioactivity of pitchblende had begun five years earlier.

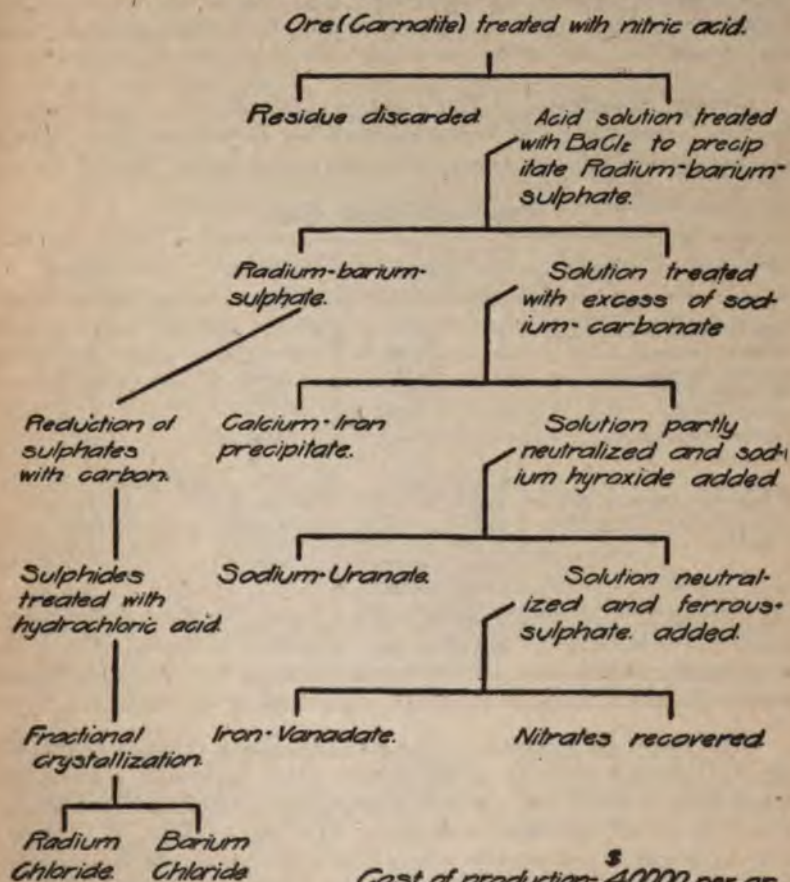
Radium occurs chiefly in pitchblende, which is found chiefly in Bohemia and Colorado. Pitchblende is an ore of uranium, containing the oxide,  $\text{U}_3\text{O}_8$ , associated with a large number of other elements. Indeed radium is always a constituent of uranium-bearing minerals and there seems to be a definite ratio between their uranium and radium content. Small amounts of radium compounds, or at least of radioactivity, are found in many rocks and varieties of mineral waters. The metal itself was first isolated in 1910 by Madame Curie and Debierne.

**Preparation, Properties, and Compounds.** — The compounds of the element were first isolated by fractional crystallization of that portion of the solution of pitchblende which does not precipitate when treated with sulfides, *i.e.*, from the analytical 4th group solution. (*Vide* p. 397.) Many crystallizations are necessary and the quantity is so small that many tons of pitchblende must be treated in order to obtain a few milligrams of the salts. (It is estimated that a ton of pitchblende contains only 0.2 gram of radium.) The element was prepared by electrolyzing the radium chloride, using mercury as a cathode. The amalgam so formed may be decomposed by heat and the mercury volatilized. The metal is white, melts at  $700^\circ$ , tarnishes in the air, decomposes water readily and in general behaves as an alkaline earth metal should. Its salts resemble in appearance and behavior those of barium, being in general slightly less soluble.



The volatile salts color the Bunsen flame bright red and the spectrum shows two red bands, a fainter blue-green band, and two weak violet lines. The equivalent

## PREPARATION OF RADIUM



Cost of production \$40,000 per gr.  
 Price in 1916 - 120,000  
 U.S. BUREAU OF MINES. BULLETIN 104.  
 SCIENTIFIC AMERICAN. Vol. 94. pg. 1914-1916.

FIG. 106.

weight, as shown by analysis of its chloride and bromide, is 113.2. If, therefore, it is bivalent as are the other members of its group, its atomic weight is 226.4.

The most characteristic property of both the element and its salts is that of giving off radiations capable of affecting a photographic plate. Associated with this property is the constant evolution of heat and the formation of disintegration products which are indicative of the decomposition of atoms. These relations are so important that special consideration of them is made in Chapter XXXIII. Its salts are prepared under the supervision of the U. S. Bureau of Mines from the Colorado ores. The method is outlined in the chart given in Fig. 106.

**Group Relations.**—The relation between the properties of calcium, strontium, and barium are shown in tabular form below. Radium is omitted since some of the data are not available.

The Alkaline Earth Metals

	Calcium.	Strontium.	Barium.
Atomic weight.....	40.1	87.63	137.37
Specific gravity.....	1.55	2.54	3.75
Atomic volume.....	26.4	38.7	36.6
Melting point.....	780°	800°	850°
Specific heat.....	0.152	.....	0.068
Flame coloration.....	Brick-red	Crimson	Green
Valence.....	2	2	2
	Ca(OH) <sub>2</sub>	Sr(OH) <sub>2</sub> · 8H <sub>2</sub> O	Ba(OH) <sub>2</sub> · 8H <sub>2</sub> O
Solubility in water of hydroxide per 100 g. of solution.....	0.131 at 0°	0.35 at 0°	1.48 at 0°
	0.113 at 30°	1.00 at 30°	3.36 at 30°
	0.067 at 80°	6.57 at 80°	48.65 at 78.5°
	0.017 at 150°		
	CaSO <sub>4</sub> · 2H <sub>2</sub> O		
Solubility in water of sulfate per 100 g. of solution.....	0.1756 at 0°	9.8 × 10 <sup>-3</sup> at 0°	1.7 × 10 <sup>-4</sup> at 0°
	0.2095 at 30°	14.8 × 10 <sup>-3</sup> at 20°	2.3 × 10 <sup>-4</sup> at 25°
	0.170 at 100°		
Solubility of carbonate.....	1.31 × 10 <sup>-3</sup> at 16°	1.00 × 10 <sup>-3</sup>	1.86 × 10 <sup>-3</sup> at 16°

**Analytical Reactions.**—The soluble salts of these three metals are not precipitated by hydrochloric acid, hydrogen sulfide, or ammonium sulfide, but are precipitated by ammonium carbonate. These facts are utilized to separate the metals from all others. The carbonates are readily soluble in acids and their separation from each other is effected by taking advantage of the relative solubilities of the sulfates, oxalates, and carbonates. (For details see texts on qualitative analysis.) All three give with volatile salts flame colorations as noted in the table, and these colorations are used for final identification. In quantitative estimation calcium is usually determined as the oxalate, strontium as the carbonate, and barium as the sulfate, since these are respectively



the most insoluble salts (for details consult quantitative texts). Radium is usually detected by use of the electroscope (*q.v.*).

**Exercises.** — 1. If an electrolytic decomposition of a calcium chloride solution were to be attempted, what is the minimum voltage needed? What difficulties would be encountered? How may they be met?

2. In the preparation of calcium phosphide from lime and phosphorus, what other substance is formed? Is it an impurity of the product?

3. Calcium chloride solutions show the solubility curve given on p. 453. What is the approximate molar concentration at the eutectic point?

4. Calcium chloride when completely dehydrated and then redissolved in water is somewhat alkaline. Why?

5. Why is the "theoretical" amount of available chlorine not found in commercial chloride of lime?

6. How much calcium oxide is formed when 5 grams of calcium carbonate is heated to  $800^{\circ}$  in a closed liter vessel until equilibrium is reached. Disregard the space occupied by the limestone or lime.

7. Calcite with a specific gravity of 2.70 changes on sufficient heating to lime with a specific gravity of 3.3. What is the volume change? (N.B. Do not neglect the weight change.)

8. When calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , is heated sufficiently it yields the oxide, nitrogen peroxide and oxygen. Formulate the molecular equation and state the ratio by volume of nitric oxide and of oxygen at a temperature of  $150^{\circ}$  and at  $27^{\circ}$  (*cf.* 294).

9. Explain by means of an equation the formation of stalagmites in caves.

10. Formulate the ionic equations for the precipitation of calcium salts by ammonium oxalate and of barium salts by sulfates.

11. Formulate the series of reactions by which sulfuric acid may be produced from gypsum.

12. Why is "reverted" ortho calcium phosphate more available for plant food than the mineral apatite?

13. Why is barium peroxide not prepared by direct heating of the barium carbonate?

14. If radium decomposes into helium and other decomposition products, why is it regarded as an element?

## CHAPTER XXVII

### GROUP II—SUB-GROUP B

THE members of this sub-group, magnesium, zinc, cadmium and mercury, do not offer the same satisfactory relationship to each other as is the case with sub-group A. (Cf. sub-groups A and B of Group I.) Magnesium compounds, like those of sodium, are very similar in their relations to those of the first member of the sub-group A, and magnesium is frequently classed as an alkaline earth metal. The metal itself is, however, similar to zinc. Zinc and cadmium are closely similar but mercury is very different, resembling in chemical behavior the copper group metals, and as an element is a curious anomaly among the metals. It is practically the only member of the group showing a variable valence.

#### MAGNESIUM

**Occurrence.**—Magnesium, the sixth element from the standpoint of quantity, is of very extensive and varied occurrence. The types of compounds are like those of calcium and the most important are the carbonate, magnesite,  $\text{MgCO}_3$ , and dolomite,  $\text{MgCa}(\text{CO}_3)_2$ ; talc, or soapstone,  $\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$ ; serpentine,  $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ; meerschaum,  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ . These are all insoluble. An indifferently soluble double chloride,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , occurs as carnallite in salt beds. The chloride,  $\text{MgCl}_2$ , and the sulfate,  $\text{MgSO}_4$ , occur in vast quantities in water. Both are constituents of sea water, and the latter of many surface waters. There are also many deposits of the sulfate which have been produced by evaporation of lakes. There are many other mineral forms containing magnesium (see texts on mineralogy).

**History.**—The salts of magnesium were not distinguished from those of calcium until 1695 when Grew described the salt  $\text{MgSO}_4$  derived from the mineral springs at Epsom, England. The carbonate came into use as a medicine about 1700, and in 1755 Black



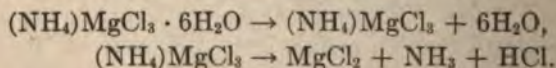
showed clearly the distinction between magnesium oxide and the oxide of calcium. The name is derived from the name of a town in Asia Minor, and is due probably to an attempt to contrast the powdered basic carbonate, "magnesia alba," with the substance which came from Asia Minor then known as "magnesia nigra" and now known as manganese dioxide. (Cf. manganese.) (The origin of these two names is not very certain.) In the classic investigation by Davy 1807, (cf Sodium) he isolated the impure metal, but its discovery is usually ascribed to Liebig and Bussey in 1830, who prepared it by reduction of the chloride by metallic potassium. The first preparation of any quantity of the metal was by Bunsen in 1832.

**Preparation and Properties.**—Magnesium is prepared in two forms, ribbon or wire form, and as a powder. It is obtained by reduction of the dehydrated carnallite by electrolysis. The molten mass is a good conductor and if the electrolysis is carried out in iron crucibles as the cathode the metal collects in globules upon the bottom. The impure metal may be purified by distillation and collected as a powder. The molten metal may be allowed to cool partially, and be drawn out to wire form and then rolled into the ribbon form in which it is frequently employed.

The metal is silver white and has a specific gravity of 1.75. It is less active chemically than calcium, yet in moist air it coats itself with a thin film of hydroxide which protects it from further corrosion. It burns with an intense white light, the temperature of which does not correspond to the intensity and there is probable direct production of light. (Cf. Chap. XXV.) The efficiency of the light is about 10 per cent. Its light is also very rich in ultra-violet and other short waves and hence for chemical purposes is about 60 times as effective as gaslight. When it burns in the air it unites with both the oxygen and nitrogen, and the presence of the nitride in the ash can be shown by the formation of ammonia by treatment with water. The metal acts as a powerful reducing agent and was so used to prepare metals from difficultly reducible oxides until its place was taken by aluminium (*q.v.*). Magnesium unites directly with sulfur, arsenic, and many other elements. In powdered form it reacts slowly with boiling water to form hydrogen but reacts very vigorously with superheated steam. It behaves as does aluminium when used as an anode and may be used as a current rectifier. (See passive aluminium.)

**Uses.** — Magnesium finds very extensive application in photography for printing purposes and as flashlight powder. The flashlight powder is a mixture of potassium chlorate and magnesium. It is also used in pyrotechnics. An especially interesting phase of this is its use in the great war as "flares" for illumination of enemy trenches. It is also used to make alloys with aluminium ranging from 10 to 25 per cent magnesium. While the use of magnesium in organic syntheses and reductions is not great in quantity it is in importance. (See Organic Chemistry, Grignard's reaction.)

**Compounds.** — The existence of an hydride of magnesium is not definitely established. The halides are all known but the only one of these of practical importance is the chloride. (It may be noted that the fluoride is markedly insoluble (7.6 mg. per liter), is fluorescent and in other ways resembles calcium fluoride (*q.v.*) The chloride,  $\text{MgCl}_2$ , is a highly deliquescent salt and occurs in sea water and almost all salt deposits. It is very soluble in water and apparently hydrolyzes partially,  $\text{MgCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2 + 2\text{HCl}$ . That such an equilibrium exists is evidenced by the rapid corrosion of iron by water containing the chloride and by the evolution of hydrochloric acid when the solution is boiled. It is mainly for this reason that sea water cannot be used as boiler water. Likewise the anhydrous salt cannot be obtained by evaporation since the crystals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , which separate out of sufficiently concentrated solutions, when heated react as indicated,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O} + 2\text{HCl}$ . The reaction is not so smooth as indicated and ordinarily the residue is a basic salt of variable composition. The anhydrous salt may be prepared by burning magnesium in chlorine (heat of formation 151,000 cal.), or by evaporation of a solution of ammonium chloride and magnesium chloride until crystallization takes place and then heating these crystals. Two successive reactions occur:



The dry salt may be sublimed in an atmosphere of hydrogen. It dissolves in water with evolution of much heat (36,000 cal.), indicating the formation of a definite hydrate. Indeed the solubility curve indicates the existence of at least 5 hydrates. (See Abegg, Vol. II, part II, p. 46.) The chloride shows an especial tendency

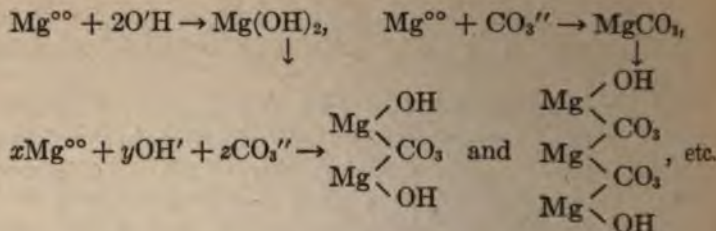


to form double salts, *e.g.*, carnallite,  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ . This salt has considerable value since it is the chief source of potassium chloride.

**Magnesium Oxide and Hydroxide.**—Magnesium oxide is readily formed by burning magnesium, but is ordinarily prepared by heating the carbonate. It is a white infusible powder which varies much according to the material from which it is prepared and the temperature employed. That from precipitated carbonate is light and porous and is known as *magnesia usta*. It is very insoluble in water, but by treatment with water is slowly transformed into the hydroxide. It is soluble in dilute acids, though the highly heated or the crystallized oxide is much less readily dissolved. It is used medicinally to a very large extent and is also used for the preparation of refractory vessels and furnace linings (*vide* basic steel, Chap. XXXV).

The hydroxide,  $\text{Mg}(\text{OH})_2$ , is prepared by treatment of the oxide with water and since both are insoluble the mass solidifies to a hard compact mass. The higher the temperature at which the oxide is prepared the less compact the solidified mass. The hydroxide is precipitated from solutions of its salts by soluble bases since the solubility is very slight, about 2 mg. per liter. It is not so completely precipitated in the presence of alkali salts, and by ammonium hydroxide is not precipitated at all, in fairly dilute solutions. The usual explanation is in terms of the ionization hypothesis, that the presence of an excess of ammonium ions depresses the ionization of ammonium hydroxide to a degree which prevents the formation of enough magnesium hydroxide to exceed its solubility. It is perhaps also due to the ready formation of the very soluble double salts, such as  $\text{NH}_4\text{MgCl}_3$ .

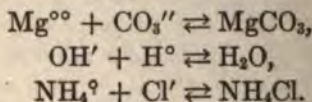
**Magnesium Carbonate.**—The normal carbonate,  $\text{MgCO}_3$ , occurs in nature as *magnesite*. It is but very slightly soluble in water. It forms isomorphous mixtures with calcite and also a double salt, *dolomite*. When solutions of magnesium salts are treated with neutral carbonates basic magnesium carbonate (*cf.* white lead) is precipitated. This is the *magnesia alba* of the pharmacist. This salt varies in composition according to the conditions of precipitation. The explanation is that the neutral carbonate in solution is hydrolyzed, *e.g.*,  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{CO}_3$ , and this system then can furnish both hydroxyl and carbonate ions to react with the magnesium ions. There are then the following possibilities:



When magnesium salts are treated with carbonates at room temperature the mixed precipitate approximates the composition  $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ , and is known as **light magnesia**. If a concentrated solution is precipitated at the boiling point the composition is more nearly  $\text{Mg}_3(\text{OH})_2(\text{CO}_3)_2$ . Whether these are other than simply mixtures of the hydroxide and carbonate does not appear from the evidence.

When the carbonate is suspended in water and carbon dioxide is passed into it the acid carbonate is produced. Like the acid carbonate of calcium it is soluble and decomposes readily with precipitation of the carbonate. The carbonate dissociates very readily when heated and the partial pressure is sufficient to effect a complete dissociation at about  $200^\circ$ .

With ammonium carbonate solutions magnesium salts are not completely precipitated and in the presence of excess of ammonium chloride are not precipitated at all. This also is explainable according to the ionization hypothesis on the basis of the relation between the three equilibria



It may also be due to the formation of soluble double salts.

**Magnesium Sulfate**,  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  ( $x = 1, 4, 6, 7$ , or  $12$ ).—The salt is found in many varieties of form, varying not only in respect to the number of molecules of water of crystallization, but as a constituent of many double salts. Of these the most important is **Epsomite**,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , which is a product of evaporation of sea water, but often is found as an efflorescence on rocks when dry. Many inland lakes which dry up in summer deposit this salt (especially in Washington and Wyoming). It is very soluble in water (269 g.  $\text{MgSO}_4$  per liter at  $0^\circ$ , 362 g. at



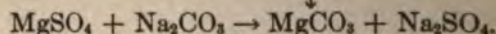
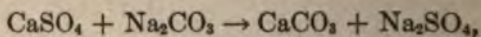
20°), and at ordinary temperature the same salt crystallizes out. At higher temperatures up to 68° the hexahydrate separates out and above 68° the monohydrate, known as the mineral kieserite, is formed. This is stable at 150°.

Magnesium sulfate is used in a large variety of industries, *e.g.*, in tanning, in dyeing, in sugar refining, in cotton printing, in the manufacture of aniline colors, etc. Its most familiar use is in medicine as a purgative. Many mineral waters are valuable chiefly because of the presence of this salt. Its presence in water is an undesirable factor when the water is used for domestic purposes and as boiler water. It is desirable, then, at this point to summarize certain points with reference to boiler scale and water softening.

**Boiler Scale.** — When water containing certain salts in solution is used in steam boilers, insoluble material is produced which interferes with the efficiency of the boilers. The formation of this material is usually due to the presence of either calcium or magnesium salts and is formed, in general, in one of three ways. (1) The acid carbonates of calcium and magnesium are decomposed by heat and the carbonates so produced settle out. (2) Calcium sulfate is fairly insoluble and as water evaporates precipitates out. This tendency is the more marked by reason of the smaller solubility at high temperature. (3) Magnesium chloride, and to a lesser extent the sulfate, hydrolyzes when heated with water and forms the hydroxide, which, with some of the salt, forms an insoluble mass. These deposits adhere, more or less rigidly, to the walls of the boilers and being poor conductors of heat entail a waste of fuel and therefore lower the steam capacity of the boilers. They also shorten the life of the boiler, due to external oxidation. In the case of the magnesium salts they also entail increased corrosion by reason of the acids liberated. In the case of the calcium sulfate and magnesium hydroxide the scale adheres firmly and is removed only with great difficulty. These and certain other difficulties render advisable the "softening" of water when these salts are present if it is to be used in boilers.

**Water Softening.** — Waters containing salts of calcium and of magnesium are called "hard" waters. (*Cf.* Chap. IV.) The hardness is of two kinds, temporary hardness and permanent hard-

ness. Temporary hardness is due to the acid carbonates of calcium and magnesium and is called **temporary** because by boiling the water the acid carbonates are converted to neutral, and insoluble, carbonates. (Iron carbonate occasionally causes hardness and is also removed by boiling, but is converted to ferric hydroxide.) These substances may also be removed by addition of the proper quantity of calcium hydroxide,  $\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$ . Permanent hardness, not removed by boiling, may be removed by addition of appropriate quantities of sodium carbonate.



Of course, soluble salts of any other acid radical which will form insoluble salts of calcium and magnesium may be, and sometimes are, used, *e.g.*, sodium silicate, sodium phosphate, etc. The method of softening varies considerably according to the local conditions but the most generally employed method is as follows: The quantity of hardness is ascertained by chemical analysis and a sufficient quantity of milk of lime, to destroy the temporary hardness and that due to magnesium salts, and of soda ash, to remove the permanent hardness due to calcium salts, is added to the water, and the precipitated carbonates and hydroxides are allowed to settle out before the water enters the boilers. Of course if only temporary hardness is to be dealt with only milk of lime is employed and conversely. Temporary hardness is sometimes removed by "pre-heating" the water. Also at times, for various reasons, water softening material may be added to the water in the boiler, the purpose being to precipitate the calcium and magnesium salts in flocculent form so that at periodic intervals the precipitate may be "blown" from the boilers. For further details the reader is referred to works on industrial or engineering chemistry. Of course, water may also be softened for domestic use, since these same factors destroy soap and impart harshness to the water. (See p. 363.)

A most interesting as well as important water softening method is that carried out by the use of "permutite," which is a trade name for the compound  $\text{NaAlSiO}_4 \cdot 3\text{H}_2\text{O}$ . If a hard water is filtered slowly through this material the sodium is displaced by the calcium and magnesium ions in solution. When the filter is ex-



hausted it may be renewed by passing through it a strong brine which reverses the reaction. The method is extensively employed.

**Other Salts.** — Of the long list of salts of magnesium the only others which need mention here are the phosphates, especially magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4$ , since it serves as a convenient means of detection and quantitative estimation of magnesium. It is formed when sodium phosphate,  $\text{Na}_2\text{HPO}_4$ , is added to an ammoniacal solution of magnesium salts since it is, of the possible salts, the least soluble. It is also used for the detection and estimation of phosphoric acid.

## ZINC

**Occurrence.** — Zinc compounds are not very abundant but are commercially important because the preparation of metallic zinc is an extensive industry. The chief ores are **sphalerite**,  $\text{ZnS}$ , **smithsonite**,  $\text{ZnCO}_3$ , **franklinite**,  $\text{Zn}(\text{FeO}_2)_2$ ; two silicates, **calamine**,  $\text{Zn}_2(\text{OH})_2\text{SiO}_3$ , and **willemite**,  $\text{Zn}_2\text{SiO}_4$ , and **zinc spinel**,  $\text{Zn}(\text{AlO}_2)_2$ .

**History.** — Zinc alloys, particularly brass, appear to have been known from the very earliest times, though without the recognition of the presence in them of a metal other than copper. The distinct recognition of the metal as a definite substance seems to be due to Paracelsus (16th century), but it was not manufactured as a separate metal in Europe until 1721 (by Henkel). It was imported much earlier from China.

**Preparation.** — The preparation of zinc by the older method consists essentially of two steps — the conversion of the ore to the oxide and the latter to the metal by reduction. The zinc is sufficiently readily volatilized so that it is distilled from the retorts in which the oxide is reduced. The zinc which first deposits in the earthenware receivers is sublimed in finely divided form and is known as zinc dust. Zinc dust is usually very impure and besides other metals contains also zinc oxide. When the receivers become warm the zinc vapors condense to a liquid which is drawn off into molds. The plates so formed are known as **spelter**. Spelter is usually quite impure, containing carbon, arsenic, cadmium and other impurities. These can be, for the most part, removed by redistillation, using various reagents to assist the process. (Abegg,

Vol. II, part II, p. 314.) Pure zinc may also be prepared by electrolytic deposition of spelter on pure zinc sheets. Zinc is also prepared by direct electrolysis of its soluble salts. This process is employed on a large scale in Great Falls, Montana.

**Properties.** — Zinc is a bluish-white metal of a specific gravity which varies according to previous treatment from 6.7 to 7.2. It is polymorphous, and besides two crystalline forms may be amorphous. Its physical properties vary therefore according to the form. The ordinary metal as it appears on the market is partly crystalline, partly amorphous. If cooled slowly from the liquid state it is highly crystalline, hard and brittle; at from 100° to 150° it is malleable and is readily rolled. Above 150° it again becomes brittle. It melts at 419° and if cooled suddenly is malleable, because amorphous. The molten zinc is denser than the solid by about 2 per cent. When molten zinc is poured into water it solidifies into irregular pieces known as **granulated** or as **mossy zinc**. Zinc boils at about 920° and the vapor density (sp. gr.) varies from 2.41 to 2.36 at 1400°. Zinc is therefore monatomic as a gas. Zinc tarnishes readily in moist air and forms a basic carbonate which adheres firmly and protects the zinc from further corrosion. When heated, zinc burns with a bluish flame, forming a fluffy white oxide (philosopher's wool). Zinc does not react with boiling water but at red heat rapidly decomposes steam. It is not readily dissolved by dilute acids, probably because the hydrogen released forms a protecting film of gas, but impure zinc is dissolved rapidly. (Cf. p. 56.) Zinc amalgamated with mercury is less rapidly dissolved by acids, since the supply of zinc on the surface is kept up by a slow process, diffusion. Zinc also is soluble in alkalis, forming zincates, *e.g.*,  $\text{Zn}(\text{ONa})_2$ . (Cf. p. 57.)

**Uses.** — Zinc is used in enormous quantities, about a million tons per year, chiefly for three purposes. In batteries, dry cells, Bunsen, Daniell and other forms; in alloys of which the chief is brass, and as a protective coating for iron. Of these the last is the most extensive. Iron so protected is known as **galvanized** iron and may be prepared by electrolytic deposition of zinc on iron (hence the name). It is much more cheaply prepared by dipping sheets of iron, carefully cleaned in sulfuric acid, in molten zinc. A third and more recent process, known as **sherardizing**, consists in heating the iron in drums at 500°–600° with zinc dust

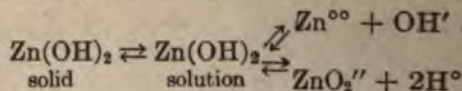


(Trans. Am. Electrochemical Soc., **21**, p. 561). Zinc is also used in sheet form for roofing purposes and for architectural ornaments. In the laboratory it finds extensive use as a means of generating hydrogen and for sundry other purposes.

**Compounds. Zinc Halides.**—While all the halides of zinc are known they offer no special points of interest except in the case of the chloride,  $\text{ZnCl}_2$ , which has been prepared in anhydrous form and also with 1, 1.5, 2, 2.5, 3, and 4 molecules of water of crystallization. In the anhydrous form it can be obtained by burning the metal in a stream of chlorine gas but not by evaporation of chloride solutions prepared by solution of the metal, oxide, or carbonate in hydrochloric acid (*cf.* magnesium). The salt is deliquescent and also very soluble (2080 g. per liter of water). It melts at  $290^\circ$  and boils at  $730^\circ$  and can be used for high temperature baths, in iron vessels. It is a caustic and antiseptic and is used for the preservation of wood, especially for railroad ties in dry, or fairly dry, regions. In this connection it functions by reacting with albumen to coagulate it. Either in solution or in the fused state it acts upon the oxides of metals to form readily fusible compounds and is therefore used as a flux in soft soldering by plumbers. The strong solution of the chloride mixed with zinc oxide solidifies to a hard compact insoluble mass which is utilized as a cement, especially in dentistry.

**Zinc Oxide and Hydroxide.**—Zinc oxide is made by burning zinc, or by heating the basic carbonate. It is also found in impure form in nature as zincite. It is manufactured on a very large scale for use as a pigment, zinc white or Chinese white. It turns yellow when hot and glows with an intense light when ignited. The ignited oxide is phosphorescent. When mixed with linseed oil it forms an excellent paint which does not blacken when exposed to sulfides. It is therefore used in vast amounts for interior work, and the so-called "enamel" paints. Vast amounts are also used in rubber manufacture, especially as a "filler" for automobile tires. It possesses antiseptic properties and hence is used as a constituent of zinc ointment. Zinc peroxide,  $\text{ZnO}_2$ , is also prepared and used in certain brands of antiseptic soaps. The oxide does not react with water to form the hydroxide, but the latter can be prepared by double decomposition of the salts. The hydroxide is amphoteric and reacts with

both acids and bases to form salts, the latter known as zincates. One of these, cobalt zincate,  $\text{CoZnO}_2$ , is known as "Rinnmann's green." Zinc hydroxide is only slightly soluble and is only slightly ionized. We may express the system



The solubility of zinc salts in ammonium hydroxide is not due to the amphoteric character of zinc but to the fact that it forms complex ammonia ions,  $\text{Zn}^{\circ\circ}(\text{NH}_3)_4$  like those of copper, silver, cadmium, cobalt and nickel (*q.v.*).

**Zinc Carbonate.**—The normal carbonate,  $\text{ZnCO}_3$ , is found in nature and may be precipitated from solutions of soluble zinc salts by sodium bicarbonate. With neutral alkali carbonates a basic salt is precipitated which varies in composition (*cf.* magnesium carbonate).

**Zinc Sulfate.**—This salt is known as white vitriol,  $2\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . It is prepared commercially by roasting sphalerite,  $\text{ZnS} + 2\text{O}_2 \rightarrow \text{ZnSO}_4$ . Like Epsom salts and the other hydrated sulfates, it can be had in several degrees of hydration and the last molecule of water is not removed at  $100^\circ$ . It is used as a medicine; in calico printing; in glue manufacture; to make lithopone (*q.v.*); in battery solutions, etc.

**Vitriols and Isomorphism.**—There are several sulfates which, like zinc sulfate, crystallize with seven molecules of water and are so related to each other that a mixture of their solutions when crystallized forms a single set of crystals. Such sets of crystals are said to be isomorphous (*isos* = equal and *μóρφη* = form). This set is called vitriols from "oil of vitriol" or sulfuric acid. The other vitriols are:

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{BeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (green vitriol or copperas),

$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  (blue vitriol).

The latter sulfate when crystallized alone is,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Such sets of isomorphous crystals are not uncommon and this relation has played an important part in the history of chemistry.



Substances are considered isomorphous when, like the vitriols, they crystallize in like crystalline forms and when crystallized together the crystals are made up of varying proportions of the components of the solutions. In general, also, crystals of a given substance will increase in size when immersed in solutions of isomorphous salts. Isomorphism was first studied by Mitscherlich in 1818, and with the result that he considered isomorphous substances as made up of **the same number of atoms combined in the same manner**. This hypothesis, usually known as the law of isomorphism, was accepted by Berzelius and used by him as a guide in the selection of atomic weights. The chemical importance of the isomorphism was over-emphasized in that it was assumed, though not by Mitscherlich, that isomorphous substances were necessarily made up of similar elements. (Mitscherlich himself said, "the crystalline form is independent of the chemical nature of the atoms and is determined solely by their number and mode of combination.") In spite of the failure to connect chemical properties closely with isomorphism, a knowledge of isomorphous relations is of practical importance, since in fractional crystallization it is obviously impossible to separate isomorphous substances. It is also possible to anticipate the character of impurities of a homogeneous material from a knowledge of the isomorphous substances. A few isomorphous groups besides the vitriols are the alums (*q.v.*), the alkali salts of phosphoric, arsenic and antimonious acid, the sulfides of silver, lead and copper ( $\text{Cu}_2\text{S}$ ), certain carbonates of calcium, magnesium, iron and manganese, the sulfates of barium, strontium and lead, etc.

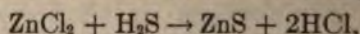
Occasionally substances which crystallize in more than one form (*e.g.*, in either the rhombic or monoclinic systems) may form two series of isomorphous salts. This phenomenon is known as **isodimorphism**.

**Zinc Sulfide.** — The sulfide of zinc is of special interest since it is the only ordinary sulfide which is white, and is the form in which zinc is isolated in the course of qualitative analysis. When zinc salts in solution are treated with ammonium sulfide,  $\text{ZnCl}_2 + (\text{NH}_4)_2\text{S} \rightleftharpoons \text{ZnS} + 2\text{NH}_4\text{Cl}$ , the sulfide formed being quite insol-

↓

uble, is precipitated. If, however, we treat solutions of zinc salts with hydrogen sulfide the sulfide is but partially precipitated, since, before it can begin to precipitate, the concentration of zinc ions and of sulfur ions must exceed the solubility product for zinc

sulfide. At the beginning we have a fairly large concentration of zinc ions and of sulfur ions but as the reaction proceeds,



the accumulation of acid, and therefore of hydrogen ions, depresses the ionization of the hydrogen sulfide to a point where  $\text{Zn}^{\infty} \times \text{S}'' < K$ , and no further formation of sulfide can occur. If to such a system in equilibrium is added a salt of a weak acid, *e.g.*, sodium acetate, the reaction  $\text{NaC}_2\text{H}_3\text{O}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HC}_2\text{H}_3\text{O}_2$ , withdraws hydrogen ions and more sulfide forms. On the other hand, if to a zinc salt a small excess of acid be added hydrogen sulfide produces no precipitate. This relation is of importance in qualitative analysis. (*Cf.* Stieglitz, *Qual. Analysis*, Vol. I, p. 204 *et seq.*) Zinc sulfide is used as a pigment but not alone. If barium sulfide is added to a solution of zinc sulfate, a mixture of barium sulfate and zinc sulfide, known as **lithopone**, results which is extensively used as a pigment. It is cheaper than white lead (*q.v.*) and zinc oxide, but is not so durable.

**Other Salts of Zinc.** — Zinc, being typically metallic in character, can of course form salts with practically all acid radicals and many of these have special application of some particular scientific interest. Their consideration lies beyond our present scope. (*Cf.* Friend, Abegg and other handbooks.) There remains only for special mention the tendency of zinc compounds to form double salts. We have a large group of double halides, cyanides, sulfides, etc., etc. (*Cf.* aluminium double salts.)

#### CADMIUM

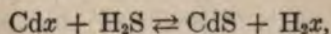
**Occurrence, History and Preparation.** — Cadmium does not occur free and is usually found associated with zinc ores, and but rarely to an extent exceeding 0.5 per cent. **Greenockite**,  $\text{CdS}$ , is the only mineral form, usually found as an efflorescence on sphalerite. The name was originally used for zinc ores and when Stromeyer in 1817 found an oxide of a new element in the flue dust of a zinc smelter he adopted the old name for the new element. It is usually prepared as a by-product in the zinc industry since the first product of the distillation of zinc ores contains most of the cadmium as a mixture of metal and oxide. This crude cadmium is concentrated by redistillation, with carbon, at a low temperature and finally by electrolysis. In the electrolysis the partially refined cad-



nium is used as an anode, cadmium chloride or sulfate as the electrolyte and pure cadmium as a cathode (*cf.* preparation of copper). Cadmium and zinc may also be separated by the precipitation of the former as the sulfide, which is insoluble in dilute acids (*cf.* zinc sulfide), and subsequent conversion of the sulfide to metallic form.

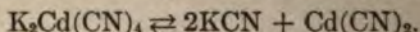
**Properties and Uses.**—Cadmium is a white metal, specific gravity, 8.54 to 8.67. It melts at  $320.2^{\circ}$  and boils at  $780^{\circ}$ . It is malleable and ductile at room temperature. It oxidizes slowly in the air, forming a thin oxide film. It burns on heating in the air. The specific gravity of its vapor is 3.94 at  $1040^{\circ}$ . Its molecule is therefore monatomic. It dissolves in acids less readily than zinc. Were it not for the use of cadmium in the manufacture of fusible alloys it would be included among the rare metals. The most important of these alloys is Wood's metal (*q.v.*), which is used in safety fuses in electrical circuits and in automatic sprinklers for fire protection.

**Compounds of Cadmium.**—The compounds of cadmium are numerous and in many cases their properties have been very carefully investigated. Since their uses are very limited only very brief mention of a few will be made. The chloride,  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ , is efflorescent and does not hydrolyze to the same extent as zinc chloride. The bromide and iodide find limited uses in photography. The hydroxide and oxide,  $\text{Cd}(\text{OH})_2$  and  $\text{CdO}$ , are formed as are those of zinc. The sulfate,  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , is not isomorphous with the vitriols. Cadmium salts form, like those of zinc, a long series of double salts of the halides, cyanides, sulfates, etc. The most characteristic compound of cadmium is the sulfide,  $\text{CdS}$ , which not only serves for the final identification of the element, but is also used as a yellow pigment. It is insoluble in water and is precipitated along with the second group metals, provided the solution is not too strongly acid. If, however, the solution is strongly acid the system,



reaches equilibrium before the solubility product of  $\text{CdS}$  is reached. Cadmium not infrequently, therefore, passes over into group III and interferes with the separation of zinc and manganese (see qualitative analysis). Cadmium ions show no amphoteric ten-

dency and hence the sulfide does not dissolve in ammonium sulfide. In the usual course of qualitative analysis (*q.v.*) cadmium and copper ions are found in solution, together with an excess of ammonium hydroxide. The failure of cadmium to precipitate as the hydroxide is, as in the case of copper (*q.v.*), due to the formation of the complex ion,  $\text{Cd}(\text{NH}_3^{\circ})_4$ , which, unlike that of copper, is colorless. When potassium cyanide is added to this solution we get a transfer of both the copper and cadmium to the negative ion, *e.g.*,  $\text{Cd}(\text{NH}_3)_4(\text{OH})_2 + 4\text{KCN} \rightleftharpoons \text{K}_2\text{Cd}(\text{CN})_4 + 2\text{KOH} + 4\text{NH}_3$ . The double cyanide is to be regarded as forming a reversible system.



In so far as  $\text{Cd}(\text{CN})_2$  is present it furnishes cadmium ions and in consequence when hydrogen sulfide is added cadmium sulfide is formed to an extent exceeding its solubility product, and hence is precipitated. Attention should be called to the existence of cadmous compounds,  $\text{Cd}_2\text{O}$ ,  $\text{CdOH}$ ,  $\text{CdCl}$ , etc., because of their analogy with the corresponding compounds of mercury (*q.v.*).

## MERCURY

**Occurrence and History.** — Mercury occurs native in some localities in pockets in the rocks, but for the most part it is found in the form of cinnabar,  $\text{HgS}$ . The chief sources of supply of mercury are Spain, Italy, Austria and California. It has been known since at least 300 B.C., when mention of it is clearly made by Theophrastus. The name hydrargyrum is from  $\text{ὑδρῶς}$  = liquid, and  $\text{ἀργυρος}$  = silver, liquid silver, which when Latinized becomes hydrargyrum, hence our symbol Hg. Mercury was well known to the later alchemists, by whom it was regarded as an element (*cf.* p. 3) representing the property of volatility. Being volatile with heat it was called mercury after the fleet-footed messenger of Jove, and was symbolized by the heralds' wand, ☿, which by the astrologers was used to indicate the planet Mercury. The fact that mercury amalgamates so readily with gold and silver and that consequently when minerals were digested with mercury and the mercury then volatilized gold and silver were obtained undoubtedly contributed largely to the widespread and long-enduring belief in the transmutation of metals and the "ennobling" effect of the action of fire on heating substances with mercury. The physiological effects of mercury and its compounds are so marked that they were carefully investigated by the iatrochemists



and hence mercury compounds played an important part in the early development of chemistry as a science.

**Preparation.**—Mercury is readily prepared from cinnabar by heating. Dissociation readily occurs and the mercury volatilizes and can be condensed in suitable receivers while the sulfur burns to the dioxide and is allowed to escape. The apparatus used for the purpose varies widely according to time and locality of production. The product obtained by direct volatilization is usually contaminated by traces of lead, zinc, cadmium or other metals and may be partially purified by filtration through chamois skin bags. In the laboratory the same result, the removal of solid impurities, is sometimes secured by filtration through paper perforated by pin holes. Removal of soluble impurities is accomplished by distillation. A frequently-used laboratory device for removal of the base metal impurities is shown in Fig. 107. The mercury is delivered in the form of a fine spray into dilute nitric acid, 5 per cent, or a solution of ferric chloride. Perfectly pure mercury may be secured by distillation in vacuo.

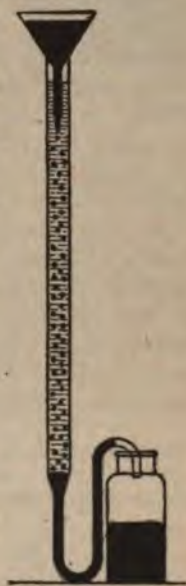


FIG. 107.

**Properties.**—Mercury is a silver white liquid metal. In thin films it is violet by transmitted light. Its specific gravity is 13.6 at 0° C. It solidifies to a malleable solid at  $-38.85^{\circ}$  of sp. gr. 14.1932. It boils at  $357^{\circ}$ . At ordinary temperatures it has a small, though measurable, vapor tension. This, coupled with its high specific weight, accounts for its use in many connections (*vide infra*). Mercury as a liquid is a good conductor of the first class. The unit of resistance, the "ohm," is that offered by 1.06 meters of mercury of a cross section of 1 mm. The vapor is a much poorer conductor (*vide infra*). The metal is not oxidized by air at room temperature nor is it attacked by acids as such. Dilute nitric acid acts slowly upon it, giving mercurous nitrate, while concentrated acid yields mercuric nitrate. It is not affected by alkaline hydroxides. The most important property of mercury is the extent to which it reacts with other metals to form alloys. These are known as amalgams. Their formation closely resembles

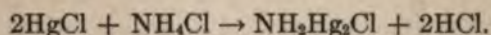
the formation of ordinary solutions. Heat in considerable quantity is frequently evolved. The freezing point of mercury is always lowered as in other solutions by small additions but at certain points in the freezing point curves there are "knicks" indicating the formation of definite compounds. In certain cases these are sufficiently stable to remain after the excess of mercury is driven off, *e.g.*, if a solution of potassium in mercury is heated to  $440^{\circ}$ , there remains a residue having the composition  $\text{HgK}_2$ . It would seem then that mercury dissolves other metals to form definite compounds and also acts as an ordinary solvent, whatever that may mean. Mercury has an atomic weight of 200. This value is derived from the molecular weight of its volatile compounds and from the combining weight, established by analysis of the chlorides, the oxide, etc. The atomic weight so reached corresponds also to that called for by the isomorphous relations with salts of copper and of lead. The vapor of mercury has a molecular weight corresponding to the atomic weight, *i.e.*, it is monatomic and the ratio  $\frac{C_p}{C_v} = 1.67$ . This is important as evidence for assuming mon-atomicity of the noble gases (*cf.* p. 278).

**Uses.**—Mercury is used very extensively as a liquid indicator of temperature, not alone because of the wide range of temperature, on each side of the normal, within which it remains liquid but because of the fairly uniform cubical expansion at different temperatures. Its great weight, and its non-corrosion in the air, render it very useful for barometers, and for pendulums, governors, etc., etc. It is used to a very great extent in metallurgy in the isolation of gold and silver. Its most extensive use is in the formation of amalgams which serve an enormous variety of purposes ranging from the coating of electrodes to prevent "local action" to the manufacture of amalgam fillings for teeth and the coating of cheap mirrors. One of the interesting uses is in the manufacture of sodium and sodium hydroxide by an electrolytic method (*q.v.*). Mercury is also used to prepare a wide variety of compounds, medicinal and otherwise.

**Compounds. The Halides.**—Mercury forms two series of compounds of very different properties in one of which the metal is univalent, in the other bivalent. Both the chlorides are valuable, the monochloride,  $\text{HgCl}$ , calomel, being prepared by pre-



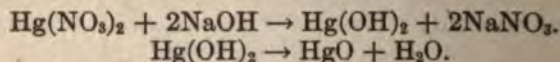
precipitation of mercurous nitrate,  $\text{HgNO}_3$ , by soluble chlorides, or by subliming a mixture of mercury and mercuric chloride,  $\text{HgCl}_2 + \text{Hg} \rightarrow 2\text{HgCl}$ . In the sunlight this reaction gradually reverses. The substance volatilizes without melting, i.e., it sublimes. The ordinary vapor density corresponds to the formula  $\text{HgCl}$ . There is some dissociation into  $\text{Hg} + \text{HgCl}_2$  and much valuable time and effort have been expended in attempting to demonstrate that mercury is always divalent and that the calomel has the formula  $\text{Cl}-\text{Hg}-\text{Hg}-\text{Cl}$  or  $\text{Hg}_2\text{Cl}_2$ . The demonstration of this much mooted but rather unimportant question still remains somewhat unsettled, but the perfectly dry salt appears to give a vapor density corresponding to the doubled formula. The substance is much used medicinally because of its purgative action and its general stimulating effect on the secretions of the body. It is also used in making standard electrodes, etc. (q.v.). **Mercuric chloride**,  $\text{HgCl}_2$ , known as **corrosive sublimate**, is prepared by heating mercuric sulphate with sodium chloride. To prevent any mercurous chloride being formed a little manganese dioxide is also added. The chloride sublimes as a white amorphous mass. Needle-like crystals may be obtained by crystallization from hot solutions. Like lead chloride the solubility of mercuric chloride mounts rapidly with the temperature. The substance is a virulent poison and coagulates albumen. The antidote is white of egg which forms with the poison an insoluble mass which is then removed from the stomach by the use of an emetic. The chloride is much used as an antiseptic for various purposes, including the washing of surgeon's hands and instruments. Usually for such purposes a solution of one part to two to three thousand of water is used. It is also frequently used as a vermifuge. Both the chlorides show a tendency to form double salts, particularly the latter, which are much used for taxidermic solutions, etc. With ammonia an interesting case of substitution takes place. With calomel we have



This is known as black precipitate. It is quite possible that the substance decomposes into the mercuric derivative and mercury, and that the black color is due to the latter in finely divided form,  $\text{Hg}_2\text{NH}_2\text{Cl} \rightarrow \text{Hg} + \text{HgNH}_2\text{Cl}$ . The last mentioned substance is

known as white precipitate and is formed when ammonia is added to mercuric salts. This behavior of ammonia with mercury compounds is not limited to the chlorides. When mercuric iodide, a brilliant scarlet powder, is treated with an excess of potassium iodide a double salt is produced,  $2KI + HgI_2 \rightarrow K_2HgI_4$  (Nessler's Solution). This is so little dissociated in the direction  $\leftarrow$  that  $Hg^0$  is with difficulty detected in the solution. With ammonia or its salts complete substitution of hydrogen by mercury takes place,  $2K_2HgI_4 + NH_4OH + 3KOH \rightarrow 7KI + 4H_2O + NH_2HgI$ , or more simply,  $2HgI_2 + 4NH_3 \rightarrow 3NH_4I + NH_2HgI$ . The latter is a very insoluble brown substance and its formation is the most delicate test for ammonia. Mercurous iodide is not stable but decomposes spontaneously into mercury and mercuric iodide. Mercuric iodide occurs in two crystalline forms, which belong to different crystalline systems. The tetragonal crystals are formed by sudden cooling of the iodide which has been heated for some time at the melting point  $223^\circ$ . On standing, or with agitation, the yellow crystals go over with evolution of heat to the more stable red, or monoclinic, variety. This is also the explanation of the change of the yellow precipitate to the red on standing. This is another instance of the principle of transformation by steps. The same difference of color, and probably the same explanation, occurs with the oxides.

**Oxides of Mercury.**—There are two oxides,  $Hg_2O$  and  $HgO$ . They are formed by precipitation of the corresponding salts with bases. Doubtless the hydroxide is first formed and decomposes spontaneously into the oxide.

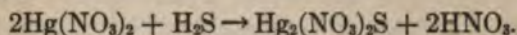


The mercurous oxide decomposes under the influence of light, or at  $100^\circ$ , into mercury and oxygen while the mercuric oxide must be heated to  $500\text{--}600^\circ$ . The mercuric oxide is formed by calcining mercury in the air,  $Hg + O \rightarrow HgO$ , at about  $350^\circ$ . This is historically a very interesting reversible reaction since the "mercurius calcinatus per se" was heated by Priestley to first prepare oxygen and the calcination itself used by Lavoisier to demonstrate the composition of the air and the nature of combustion. (Cf. p. 26.) Both the red and yellow oxides are used in pharmacy. The yellow variety is formed by precipitation of mercuric salts with bases and



changes to red on heating; hence the name sometimes employed, "red precipitate."

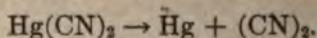
**Sulfides of Mercury.**—**Mercurous sulphide** is unstable and at temperatures of  $10^{\circ}$  or above breaks down spontaneously into mercuric sulfide and mercury. Crystallized **mercuric sulfide** occurs in nature as cinnabar and may be formed by subliming the black sulfide formed by precipitation. The red variety is clearly the stable and the black the metastable form. Both forms are extremely insoluble in water or acids but with nascent chlorine (aqua regia), or other oxidizing agents, sulfur is displaced and more readily soluble compounds produced. The red form is used under the name vermilion as a pigment and is more stable and brilliant than red lead since it is not so readily affected by atmospheric conditions, but is not suitable for iron or other metallic structures by reason of the place of mercury in the electromotive series (*q.v.*). The sulfides of mercury show a tendency to form complex insoluble salts during precipitation, which are of various colors. For example, if mercuric nitrate is treated very slowly with hydrogen sulfide a series of precipitates may form, varying from white to yellow orange and black. The colors are due to partial transformation to sulfide, *e.g.*,



(*Cf.* magnesium basic carbonate.) The formation of sulfides by treatment of soluble salts with hydrogen sulfide is itself a secondary reaction analogous to that of the decomposition of the hydroxides. Hydrogen sulfide being a weak dibasic acid may be considered as ionizing only to  $\text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}'$ . With mercury ions we should then expect  $\text{Hg}(\text{HS})_2$ , but instead we get  $\text{Hg}(\text{HS})_2 \rightarrow \text{HgS} + \text{H}_2\text{S}$ . This is wholly analogous to the general behavior of hydroxides, with the difference to be expected that the sulfhydrides are uniformly less stable than the hydroxides.

**Mercuric Cyanide and Other Nitrogen Compounds.**—The cyanide is fairly soluble in water. It is formed by treating fresh mercury oxide with hydrocyanic acid. It is a poison and hence a good antiseptic. It has come recently into extensive use as an antiseptic for surgeons' hands and instruments, the reason being that in solution it is so very little ionized that no displacement of the mercury by the metals of the instruments takes place. With two such poisonous factors as mercury and cyanogen, it might be expected to be virulently poisonous, but, probably by reason of its

slight ionization, it is less poisonous than corrosive sublimate. Mercuric cyanide when heated yields cyanogen.



The corresponding sulfocyanate,  $\text{Hg}(\text{CNS})_2$ , is used for the manufacture of the toy "Pharaoh's Serpents." Apparently the sulfur present burns and by reason of the low temperature, maintained by reason of the escape of nitrogen, the kindling temperature of carbon is not reached. A voluminous mass of carbon and mercury remains. Fulminating mercury, so extensively used in the preparation of percussion caps for cartridges, shells, dynamite, etc., is made by treating mercuric nitrate with alcohol. It is mercuric isocyanate,  $\text{Hg}(\text{CNO})_2$ .

**Other Salts of Mercury.** — Of course, a wide variety of other salts of mercury exist and find more or less varied applications. The **nitrates**  $\text{HgNO}_3$  and  $\text{Hg}(\text{NO}_3)_2$  are usually the starting point in the demonstration of the properties of the mercuric and mercurous ions. The **carbonates** readily yield carbon dioxide, oxygen and mercury on heating. Mercurous sulfate,  $\text{Hg}_2\text{SO}_4$ , is used in the preparation of standard cells of the Weston type. Mercury forms a large number of complex compounds of the "molecular" type and especially with ammonia. These have been investigated, particularly by E. C. Franklin. They are of particular interest because they emphasize the analogy between ammonia and water as reagents.

## BERYLLIUM

**Occurrence, History and Preparation.** — The element beryllium occurs in the mineral beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , of which varieties are the jewels, emerald, the color due to traces of chromium, and aquamarine. Other mineral forms are **chrysoberyl**, or cat's eye,  $\text{Be}(\text{AlO}_2)_2$ , **phanacite**,  $\text{Be}_2\text{SiO}_4$ , and other still rarer forms. It was first isolated by Wöhler in 1828, by reduction of the chloride by potassium, but the recognition of a new "earth" in beryl was by Vauquelin in 1798. The name glucina (from γλúκος = sweet) was given it by reason of the fact that its soluble salts have a sweet taste. The term beryllia for the oxide and of beryllium for the element have almost entirely displaced the older terms, though we still encounter the symbol Gl. It is also prepared by electrolysis of the chloride (cf. magnesium). Because of the similarity of the behavior of the oxide and hydroxide of beryllium with those of aluminium, it was supposed to be a trivalent element and since its equivalent weight is 4.55 its atomic weight was sup-



posed to be 13.6. This seemed especially reasonable since its specific heat is at 100° about 0.425, which by Dulong and Petit's law gives a product of  $0.425 \times 13.6 = 5.88$ , a value fairly close to the atomic heat mean (see p. 108). There was, however, a vacant space in series 1 of the periodic system for a bivalent element ( $2 \times 4.55$ ) and Mendelejeff did not hesitate to assign beryllium to this place, a conclusion confirmed when in 1884 Nilson and Pettersson showed the vapor density of the chloride to be at high temperatures (842°) 2.793.

**Properties and Uses.**—As the preceding paragraph would imply, the element has properties which relate it, not only to members of the second, but also to the third group. It is a hard bright metal, malleable and more stable in the air than is magnesium. It is soluble in acids, except nitric acid (*cf.* aluminium). Its hydroxide is weakly acidic in nature (*cf.* aluminium), and dissolves in strongly basic solutions, but it reprecipitated by boiling. Its salts readily hydrolyze (*cf.*  $MgCl_2$ ). Its carbonate is unstable both towards heat and in aqueous solution. Its salts give no color to the Bunsen flame nor to the borax or phosphate bead. In general, the metal and its salts find no uses other than that mentioned above, as gems. This fact is probably due, not to the lack of valuable properties so much as to the rarity of its natural forms and the cost of preparation of artificial ones. It is the least abundant and also the least known of the elements of the first series of the periodic system.

**Analytical Relations.**—All the metals of the sub-group form colorless ions. None of them form colored phosphates or borates and hence give no bead test (*cf.* p. 305 and p. 380). Magnesium forms only bivalent ions and its double salts all show the presence of the positive ion. While its carbonate is insoluble in water, it is soluble in the presence of ammonium salts (*cf.* p. 472) and this fact distinguishes magnesium compounds from those of the calcium family. The mixed salt, magnesium ammonium phosphate, is the least soluble salt, at least when ammonium salts are present, and is used for the detection and estimation of the element.

	Beryllium.	Magnesium.	Zinc.	Cadmium.	Mercury.
Atomic weight....	9.1	24.32	65.87	112.4	200.6
Specific gravity....	1.85	1.75	6.9-7.2	8.6	13.5956
Atomic volume....	4.9	13.9	9.29	13.0	14.9
Melting point.....	1000°	651°	419°	320.2°	-38.85°
Boiling point.....		1120°	916°	780°	357.3°
Specific heat.... {	0.3756 at 0°	0.2456 at 0°	0.0907	0.0555	0.039
	0.6206 at 500°	0.2519 at 50°			

Zinc ions are distinguished by the fact that while with sulfide ions, zinc sulfide is formed, the sulfide is soluble in dilute acid. Mercury and cadmium both form

sulfides insoluble in water and dilute acids, the latter being more readily soluble. In the case of mercurous ions, with both chloride and sulfate ions insoluble salts are formed.

Beryllium sulfide is hydrolyzed by water and the hydroxide is formed along with those of the third group. Its nearest analytical relation being aluminium, from which it is distinguished by the fact that on boiling, the beryllates, *e.g.*,  $\text{Be}(\text{ONa})_2$ , are hydrolyzed, while aluminates are not. It will be seen, then, that mercurous salts relate themselves to the first analytical group (see p. 396), mercuric salts and those of cadmium to the second group, beryllium and zinc to the third.

**Exercises.** — 1. Formulate the reactions which take place between magnesium chloride and water and iron in a steam boiler. What are the ultimate components of the scale formed?

2. Magnesium forms double salts and yet these show the characteristic reactions due to magnesium ions. Explain.

3. Why can we not determine definitely whether basic carbonates of magnesium are pure compounds?

4. Suppose water to contain 450 parts per million of calcium carbonate. How much slaked lime,  $\text{Ca}(\text{OH})_2$ , per thousand gallons of water would have to be used to just soften the water? In case the water contained also 250 parts per million of calcium sulfate,  $\text{CaSO}_4$ , how much sodium carbonate should be added per thousand gallons? Assume that a gallon of water weighs 8.35 lbs.

5. Compare the physical and chemical properties of magnesium with those of calcium and zinc. To which of these is magnesium more nearly related? Give your reasons in full.

6. Given a solution containing magnesium, cadmium and zinc salts, how could you prepare from it samples of pure oxides of each metal?

7. 59.20 grams of mercuric oxide yield 54.82 grams of mercury. The weight of mercury vapor per liter under standard conditions is 8.923 grams. The gram molecular volume of mercury compounds containing the smallest amount of mercury contains two hundred grams. Calculate the formula of mercuric oxide, the atomic weight and the molecular weight of mercury.

8. Review the properties of dilute nitric acid and then formulate its reactions on mercury and on zinc.

9. Formulate the reactions between zinc chloride and the acid and neutral carbonates of sodium and explain why, with the latter salt, basic carbonates are formed.

10. How do solid isomorphous mixtures of two salts differ from double salts? From a mixed salt?



11. Gold leaf suspended over mercury but not in contact with it becomes amalgamated. Why?

12. Zinc may be precipitated practically completely from zinc chloride solutions by hydrogen sulfide if sodium acetate be added in sufficient quantity. Formulate the reactions and state three other salts which might be used instead of an acetate and why they would effect the same result.

13. If the vapor density of beryllium chloride is 2.793 and the equivalent weight of this element is 4.55, calculate the maximum atomic weight of the element and state its valence. What other evidence of its valence is available?

14. Beryllium carbonate hydrolyzes somewhat in the presence of water. Why? Formulate the equilibrium.

## CHAPTER XXVIII

### ELECTROCHEMISTRY

THE frequent references in previous pages to the relation between chemical activity and electrical energy have to a certain degree indicated its importance in the study of chemistry. As with other forms of energy, electricity may be either produced or absorbed during chemical change and it is therefore possible to consider the relation from this point of view. We may define electrochemistry as the topic which deals with the facts, generalizations and theories concerning the conversion of chemical energy into and from electrical energy. In the subsequent discussion of this topic we shall use the terms which have come into use largely through the application of the hypothesis of ionization (*q.v.*) and shall leave to a later chapter the discussion of the nature of electrical energy (*vide* Electron Theory).

**Electrical Relations.** — Chemical changes which liberate energy in any form are usually spontaneous (p. 42) and we ascribe the source of the energy to the transformation of chemical energy into some other form. Under ordinary circumstances the freed energy appears in the form of heat. Under special circumstances it may wholly or in part appear as light (p. 445) or as motion (p. 352). Under proper circumstances likewise chemical energy may be converted, wholly or partially, into electrical energy. Such reactions may be called exoelectrical and are a special variety of the general type of exothermal changes. As with exothermal changes in general, so exoelectrical changes may be either synthetic or decomposition processes. The importance of exoelectrical changes to chemistry is perhaps less than that of the converse by reason of the recent enormous development of electrochemical industry utilizing electrical energy which is produced by means other than chemical, (*e.g.*, from water or steam power); exoelectrical processes are not only vastly useful, in many directions in technical ways, but are especially important because of their



relation to the development of both electrical and chemical theory (*vide infra*).

**History.** — Despite a few isolated earlier observations, the development of electricity through chemical change may be said to date from the observation by Galvani, in 1790, that frogs' legs connected at two different points by means of a metal conductor contracted sharply, especially when the conductor was made up of two different metals. The first real development followed, however, from the invention of the voltaic pile by Volta, in 1799. This consisted of a series of alternate pairs of copper and zinc plates separated by cloth moistened with sulfuric acid or salt water. (Fig. 108.) After some years the source of the electrical energy was shown, chiefly by Faraday, to be the conversion of the zinc into sulfate. The use of the pile by Berzelius (1803 *et seq.*) and by Davy (1806 *et seq.*) in endoelectrical reactions stimulated very greatly the study of electrochemical reactions.

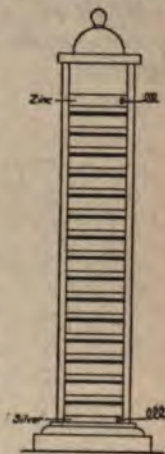


FIG. 108.

The attempt to detail the historical steps leading to our present knowledge and views would involve much discussion and may well be deferred until the student takes up the study of electrochemistry as a special topic, except so far as these steps are revealed in the subsequent topics, or have been already mentioned (p. 167).

**The Measurement of Electrical Energy.** — As already mentioned (p. 77) it is convenient to resolve the various sorts of energy, where possible, into two factors such that their product represents the total energy. The intensity factor determines whether a transference of energy will take place; the quantity factor determines to what extent. The quantity factor of electricity is usually expressed in **coulombs**, the intensity factor in **volts**, and the total energy, coulombs  $\times$  volts, in **joules**. If we wish to express **rate of transfer** of electrical energy we use the terms **ampere** (= 1 coulomb per second) and **watt** (= 1 joule per second). (*Cf.* p. 169.) Any instrument which by passage of an electric current registers the number of coulombs, or fractions thereof, passing per second is called an **ammeter**, and the usual device for this purpose is illustrated in Fig. 109.

Similarly any device which registers the difference of potential, E.M.F., between two points in an electrical circuit is known as a voltmeter. (Fig. 110.) (For details of construction of these instruments consult physics text-books.)

If we desire to ascertain the quantity of electricity without reference to time, the instrument employed is called a coulometer. (Fig. 111.)



FIG. 109.



FIG. 110.

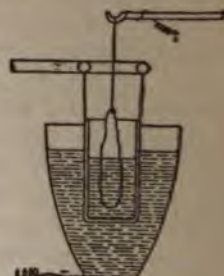


FIG. 111.

**The Voltaic Cell.**—When zinc is treated with copper sulfate the reaction indicated is  $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu} + 209,910$  joules. This energy evolution ordinarily manifests itself as heat, but if we arrange the conditions properly we may, instead, obtain electricity. Thus, we may place a plate of zinc in zinc sulfate and of copper in copper sulfate, as indicated in Fig. 112, and if the zinc and copper

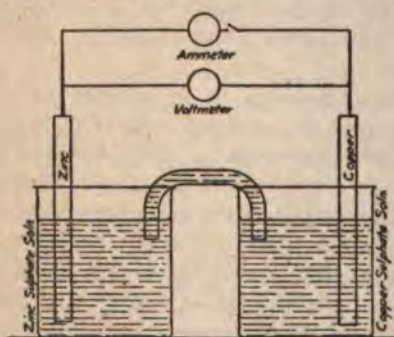


FIG. 112.

are connected externally by a conductor (cf. p. 166), and through an ammeter, a current flow will be indicated, and if by means of a voltmeter the current intensity be measured it will be found that when 65 g. of zinc have gone into solution and 63.6 g. of copper are deposited the total energy liberated in electrical form is almost exactly 209,910 joules (i.e., 1.0962 volts times 196,540 coulombs = 215,447.

Any arrangement by which the chemical energy of a reaction may be so converted into electrical energy is called a **voltaic cell**. It does not follow always that as in the above case, the Daniell cell, the transformation is so nearly exact. On the



contrary, such is seldom the case because part of the energy may be liberated in the form of heat, in which case the cell rises in temperature while delivering current, or it may be that as the cell works external energy in the form of heat is also converted to electrical energy and the temperature of the cell falls, as is the case in the Daniell cell. Cells may therefore have either a positive or a negative heat coefficient.

Voltaic cells are variously classified according to convenience, and it will suit our present purpose to consider two types, the displacement cell and the concentration cell.

**The Displacement Cell.** — We have seen that the order of the metals is the same when we consider the rate at which they displace hydrogen from water or from acids so far as they do so at all (p. 54 *et seq.*). We have also seen that when the metals are arranged in the order in which they will displace each other from their salts we get the series given on page 390. When we consider these elements with reference to thermal relations we find that the heat of formation of a given salt is greater the higher the metal in the series, and that in the displacement of one metal by another the heat liberated is the greater the farther apart the metals in the series. It follows, then, that if we can arrange the reactions so that a part or all of the energy can be converted to electricity that any displacement reaction can be made to furnish a voltaic cell. This result can be secured if the arrangement be as indicated in Fig. 113.

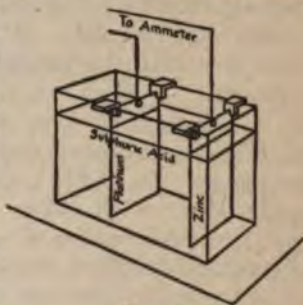


FIG. 113.

Every cell must consist of two electrodes connected externally by a conductor of the first class and internally by one of the second class (p. 166). The total electrical energy delivered will depend upon the "heat of formation" of a given compound, less that which is converted actually into heat. The rate, *i.e.*, the E.M.F., will depend on the relative positions of the elements functioning in the reaction. The explanation of these relations in terms of the ionization hypothesis (*q.v.*) is as follows:

**The Nernst Hypothesis.** — The metals possess an inherent tendency to go into solution as ions, *i.e.*, they have a solution

tension. This tendency is greatest in the case of caesium and least in the case of osmium. When metals go into solution

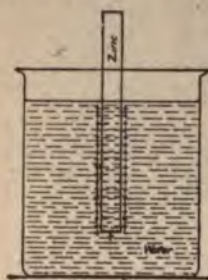


FIG. 114.

ionic charge is positive. In the case of non-metals there is also a solution tension but the ions formed are negative, and the tendency is least with silicon and greatest with fluorine. From Faraday's laws (p. 167 and 172) it follows that the ionic charge is the same as the valency. When, then, a metal is placed in water a solution tends to form consisting of free ions of the metal; but soon equilibrium is reached, due to the charge developed on the residual metal. For example with zinc and water we may picture the situation as in Fig. 114. The zinc is negatively charged and the solution surrounding it is positive. It follows then that when we have a solution already containing zinc ions they have a tendency to separate out as metallic zinc and according to the osmotic theory this tendency should be greater as the concentration of zinc ions increases. This is called the **precipitation or deposition pressure**. If then we immerse a zinc stick in a solution of zinc sulfate we have an equilibrium set up between these opposing tendencies  $Zn \rightleftharpoons Zn^{++}$ . The same remarks apply also to all other metals. If now we have a concentration of ions of a given metal of greater deposition pressure than corresponds to the solution pressure of the same metal it follows that were the metal immersed it would become coated with charged metal ions (see Fig. 115). This hypothesis is known as the **Nernst solution hypothesis** (first announced in 1889).



FIG. 115.

**Single Potentials.** — In fact, if any metal is immersed in a solution normal with respect to its salt it is possible to measure the potential by means of the device shown in Fig. 116 (a calomel electrode against a single electrode). (In making such measurements it is first essential to secure a basis of comparison. There has been considerable difference of opinion as to what is the most convenient zero point and no absolute uniformity of usage yet



obtains. On the basis of the above hypothesis a hydrogen electrode (*vide* electrochemistry texts) should have a potential of zero and in the following considerations is taken as such.

Measured against a hydrogen electrode a calomel electrode (A in Fig. 116) gives a potential of  $-0.283$  volts. The calomel electrode is made up of metallic mercury covered by calomel ( $\text{HgCl}$ ) and a normal solution of potassium chloride. It is essentially half a cell and when connected with another electrode, as indicated, and the E.M.F. of the combination determined,

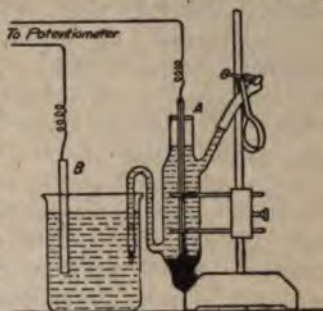


Fig. 116.

the potential of the single electrode can be determined. In this way the potential developed by various elements in normal solutions of their salts have been determined and are as given in the following table:

## Electrode Potentials

Cs.	Co.....	-0.232	Rd.
Rb.	Ni.....	-0.228	Os.
K..... - (3.18)	Sn.....	-0.192	<i>Non-metals</i>
Na..... - (2.82)	Pb.....	-0.148	Si.
Li.	H.....	0.000	C.
Ba..... - (2.81)	Sb.		B.
Sr..... - (2.76)	Bi.		N.
Ca..... - (2.55)	As.....	+0.29	Se.
Mg..... -1.48	Cu.....	+0.329	P.
Al..... -1.276	Hg.....	+0.750	S.
Cr.	Ag.....	+0.771	I..... +0.520
Mn..... -1.075	Pd.		Br..... +0.993
Zn..... -0.770	Pt.....	+0.863	O..... +1.23
Cd..... -0.420	Au.....	+1.079	Cl..... +1.417
Fe..... -0.340	Ir.		F.
Tl..... -0.322			

Where in the above table no values are given no accurate data on electrode potentials are available, but the position of the elements is that arrived at from other data. The potentials of the more active metals (those bracketed) and of the non-metals, are also not directly determined. The values are in no case accurate to the third decimal place.

A voltaic cell, then, considered as a machine for converting chemical energy directly to electrical energy, will work whenever

we have two electrodes of different potential immersed in an electrolyte and connected externally so that the unequal potentials can cause a movement of electrical energy and will continue to work so long as the difference of potential is kept up by the chemical changes taking place. The potential of the cell should therefore be the algebraic difference of the potentials of the electrodes. Thus in the Daniell cell  $\text{Zn}-\text{ZnSO}_4-\text{CuSO}_4-\text{Cu}$ , we have zinc with a potential of  $-0.770$  and copper  $+0.329$ , or  $1.099$ , the directly measured potential of the cell being  $1.0962$ . Where two electrodes have the same sign the potential is that of the difference between them. Thus a displacement cell of  $\text{Zn}-\text{ZnSO}_4-\text{CdSO}_4-\text{Cd}$  will have an E.M.F. of  $-0.770 - (-0.420) = -0.35$  volt and the current will flow from the cadmium through the wire to the zinc and cadmium be deposited, while in the  $\text{Cd}-\text{CdSO}_4-\text{CuSO}_4-\text{Cu}$  cell the voltage will be  $-0.420 - (+0.329) = -0.749$  and the current flow from the copper to the cadmium, and copper is deposited. In general the magnitude of the potential of a cell is the greater the farther the metals are apart in the electromotive series and is not affected by the size or shape of the electrodes nor by the amounts of the solutions.

**Influence of Concentration.**—It follows from the Nernst hypothesis that since cell potential is determined by the equilibrium between the solution and deposition pressures that the more concentrated the solution of a salt the smaller should be the negative potential and the greater the positive potential of an electrode which is immersed in it. Thus, silver in a normal solution of a silver salt has a potential of  $+0.771$  and in an  $N/10$  solution  $+0.713$  volt and in an  $N/100$  solution  $+0.655$  volt.

Indeed Nernst has shown that in general  $\pi = \pi_0 + \frac{0.058}{n} \log \frac{1}{C}$ ,

where  $\pi_0$  = potential in normal concentration,  $n$  = the valence of the electrode material and  $C$  the concentration in equivalents of the electrolyte. (For the derivation of this formula see texts on electrochemistry.)

**Polarization.**—When a cell is made of two electrodes and one electrolyte each electrode of course develops electromotive force. Thus a cell  $\text{Zn}-\text{H}_2\text{SO}_4-\text{Pt}$  develops, when first connected up, an E.M.F. of more than 1.5 volts, but it speedily drops back to less than half a volt. This is due to the deposition of a film



of hydrogen upon the platinum which not only substitutes a hydrogen electrode in fact for the platinum but also increases the internal resistance of the cell. This is called polarization (see also electrolysis, p. 172) and can be lessened by surrounding the positive electrode of the cell by a consumer of hydrogen. This is accomplished in the Bunsen cell,  $\text{Zn} - \text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{C}$ , by placing the cathode in concentrated nitric acid in a porous cup. The nitric acid oxidizes hydrogen. In the bichromate battery the same function is performed by the chromic acid. In the Leclanché or dry cell the depolarization is performed by manganese dioxide which surrounds the carbon cathode. (See p. 417.) In such cells as the Bunsen or other "direct action" cells conversion of chemical to heat energy is partly inhibited by amalgamation of the active electrode.

**Influence of Temperature.**—The influence of temperature on a cell is that which is to be expected from the theorem of Le Chatelier. If a cell converts a part of the chemical energy into heat its temperature will rise during operation and consequently if such a cell be heated its potential will diminish and have a negative heat coefficient. In the case of the Clark cell,  $\text{Hg} - \text{Hg}_2\text{SO}_4 - \text{ZnSO}_4 - \text{Zn}$ , the potential of which is 1.4328 v. at  $15^\circ$ , decreases about 0.0012 volt for each degree rise in temperature. In the case the cell lowers in temperature while working, increase of temperature increases the potential, and the cell will have a positive heat coefficient. Such cells are less common than those with negative coefficient. The cell  $\text{Cu} - \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{Pb}$  has a positive coefficient of +0.0004 v. per degree. The Daniell cell has a positive heat coefficient of 0.00003 v. per degree. Potential measurements of cells are usually made by comparison with a known cell by means of a potentiometer or similar instrument. (See Physical Measurement texts.) It is therefore convenient to have as a standard basis of comparison a cell which has a constant potential and with but a small tempera-

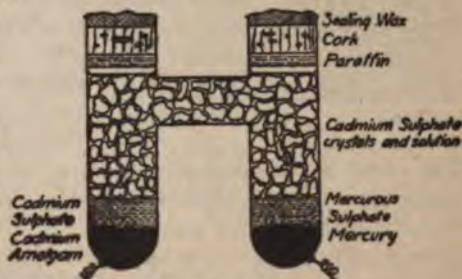


FIG. 117.

ture coefficient. The one most commonly employed is the Weston cell (Fig. 117), which is  $\text{Hg} - \text{Hg}_2\text{SO}_4 - \text{CdSO}_4 - \text{Cd}$ . It has an E.M.F. of 1.0183 at  $20^\circ$  and a negative heat coefficient of 0.00004 v. per degree.

**Quantity Factor.** — It will have been observed that each element as it undergoes a chemical change gives rise to a definite quantity of electrical energy and that the intensity, the electrode potential, varies with the different elements. In a similar manner the quantity factor, the number of coulombs, varies with the quantity of material undergoing chemical change. It is, however, important to note that there is a definite relation between this quantity and the equivalent weights of the elements. An equivalent weight of any metal on becoming ionized furnishes exactly the same quantity as any other, viz. 96,500 coulombs, which quantity is called a **Faraday**. The total energy is different since the potentials of the elements vary. The rate at which the current is produced can be varied by varying the surface exposed to the chemical action or by any other condition which influences the rate of action.

**Concentration Cells.** — If two rods of zinc be immersed in a solution of a zinc salt of the same concentration and connected through a voltmeter no difference of potential should be observed, because the two equal forces are acting in opposite directions. If, however, the concentration of the solution around the two electrodes is different a voltaic cell should be produced as already noted on p. 391. The potential of such a cell can be calculated from Nernst's formula, p. 498, remembering always that the two poles are opposed.

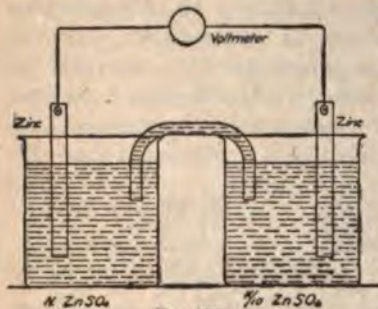


FIG. 118.

The most interesting consequence of this relation is that it furnishes a means of calculation of the concentration of a salt in very dilute solution. For example, if a silver electrode be placed in a normal solution of silver salt and electrically connected as in Fig. 118, with a solution of silver chloride the magnitude of the potential makes possible at once the calculation of the concentration of the silver ions in the dilute solution. This method has proved more accurate than direct measurement of solubilities.



Another consequence of the concentration cell is that it shows the order of the elements in the displacement series (p. 497) to depend not only upon the relative order of the metals, but also upon concentration, since it follows that as the concentration of a solution with respect to a given ion decreases the potential of an electrode of the same material increases. Thus, while in the electromotive series arsenic precedes copper, yet if copper be immersed in strong solution of an arsenic compound the positions are reversed and arsenic is precipitated. This is known as Reinsch's test (see qualitative analysis). Another case illustrating the same point: zinc or iron displaces copper ions from solutions of copper salts under ordinary conditions, but in the solution of  $K_2Cu(CN)_4$ , where the concentration of copper ions is exceedingly small, no displacement is effected. Indeed the order may be reversed and both copper and iron will precipitate zinc from  $K_2Zn(CN)_4$ . From consideration of the temperature coefficient it will be evident that the order of the elements may also vary somewhat with change of temperature.

**Couples.**—It follows from the above considerations that if a metal while reacting with acid, or other reagent capable of converting it into ionic form, is in contact with another element below it in the electromotive series we have a voltaic cell and the rate of reaction is increased, since the movement of the electric current tends to carry the ions from its surface and so diminish the deposition pressure. Also gaseous or other deposition on its surface is lessened since they tend to deposit on the less active metal. We have in the relation an explanation of the "catalytic" effect of copper and platinum, mentioned on p. 56, and also of the lesser stability of metals which are impure. We also have through it an explanation of the protection of iron in boilers and otherwise by means of zinc, since zinc is higher in the series than iron and is sacrificed to save the iron. Another example is furnished by the more rapid rusting of **tinware**, iron coated with tin, when the surface is broken. Tin is lower in the electromotive series than is iron.

#### ENDO ELECTRICAL RELATIONS

Reactions of a chemical sort are frequently accomplished by utilization of electrical energy. These reactions may be called **endoelectrical**, and, like their converse, may be either synthetic or

decomposition processes. Certain phases of these have already received somewhat extended treatment and the student is requested to review what has already been said concerning the laws of Faraday, (p. 167), the general facts of electrolysis (p. 168 *et seq.*), the hypothesis of Arrhenius (p. 171 *et seq.*), the amounts of electricity upon the ions (p. 172), equilibrium in electrolytes (p. 173), and the degree of ionization (p. 174). It is the present purpose to make a few more extended observations concerning some of these topics and add a few others in the interest of a more complete survey of the general topic.

**The Coulometer and Ammeter.** — When an electrical current is passed through certain substances decomposition takes place. These substances are known as conductors of the second class, or as **electrolytes**, and the process of decomposition as **electrolysis**. The products of decomposition appear only at the points where the electricity enters and leaves the solution. These points are called **electrodes**. By convention the point of ingress of the current is assumed to be at that electrode which is connected with the positive pole of the source of current, the **anode**, and of egress at the electrode connected with the negative pole of the source of current, the **cathode**. As was shown by Faraday, the amount of decomposition which takes place depends solely upon the quantity of electricity which passes through the electrolyte. The most exact measurements have been made on silver salts and it appears that one coulomb deposits 0.0011175 g. of silver, and of course an equivalent amount of the other portion of the salt. The equivalent weight of silver is its atomic weight and consequently to deposit a gram equivalent of silver would require  $\frac{107.88}{0.0011175}$  or 96,540 coulombs.

This quantity, called a **Faraday**, will then liberate an equivalent weight in grams of any substance. The equivalent weight of oxygen is 8 and so were oxygen liberated by the current one coulomb would liberate  $\frac{8}{96,540} = 0.000083$  g. The equivalent weight of copper

in copper sulfate is 31.8 and the electrochemical equivalent of which is therefore  $31.8 \div 96,540 = 0.0003294$  g. It is therefore possible to determine the quantity of electricity which passes through a solution by measuring the quantity of material decomposed. Any instrument suitable for this purpose is called a **coulometer** (coulomb-meter). The instrument shown in Fig. 4 is an example.



Ordinarily, however, it is more convenient to use a copper or a silver coulometer. (For the construction of such instruments consult text on physical-chemical measurements.) If the number of coulombs of electricity which pass through a coulometer is divided by the time in seconds the quotient is the rate of flow and is expressed as amperes, *i.e.*, one coulomb per second is one ampere.

**Polarization and Decomposition Potential.** — Although equal quantities of electricity deposit equivalent quantities of the ions, it does not follow that equal quantities of energy are expended, since there are required certain minimum potentials for different electrolytes and the total energy expended is the product of the quantity, coulombs, times intensity, volts. The matter can be made clear by a consideration of the following example: If two platinum plates are inserted in a solution of concentrated hydrochloric acid and connected through a voltmeter no potential is indicated. If now the two plates be connected with a source of current of about one volt, say a Daniell cell, it will be found that at first a current passes but speedily decreases nearly to zero. This is assumed to be due to the separation of hydrogen on the cathode and of chlorine on the anode, which themselves act as sources of potential and make a voltaic cell,  $H-HCl-Cl$ , with an electromotive force acting in opposition to that of the impressed current. That such a counter electromotive force exists can be demonstrated by cutting out the Daniell cell and joining the electrodes through a voltmeter. Moreover, examination of the plates will show the presence of a film of gas on each. This production of a back electromotive force during electrolysis is called **polarization**. (The same situation exists when any electrolyte is decomposed except that the magnitude of the back electromotive force will vary according to the material deposited.) If now a current of higher potential is passed through the cell the polarization increases until the electrodes are saturated with the gases and further decomposition results in the elimination of the products. This represents the maximum polarization value and the minimum **decomposition potential**. For hydrochloric acid this is found to be 1.36 volts. When a current of less potential is used with the concentrated acid the back electromotive force almost completely stops the current. The minute current, called the **residual current**, which continues to pass is that needed to maintain the polarization, since if no

current at all passes the plates would gradually depolarize. The decomposition voltages of certain normal aqueous electrolytes are shown in the following table:

Decomposition Potentials

	Volts.		Volts.
ZnSO <sub>4</sub> .....	2.35	H <sub>2</sub> SO <sub>4</sub> .....	1.67
ZnBr <sub>2</sub> .....	1.80	HNO <sub>3</sub> .....	1.65
NiSO <sub>4</sub> .....	2.09	H <sub>3</sub> PO <sub>4</sub> .....	1.70
NiCl <sub>2</sub> .....	1.85	HClO <sub>4</sub> .....	1.69
Pb(NO <sub>3</sub> ) <sub>2</sub> .....	1.50	HCl.....	1.31
AgNO <sub>3</sub> .....	0.70	HBr.....	0.95
CdSO <sub>4</sub> .....	1.98	HI.....	0.52
CdCl <sub>2</sub> .....	1.88	NaOH.....	1.69
CoSO <sub>4</sub> .....	1.92	KOH.....	1.67
CoCl <sub>2</sub> .....	1.78	NH <sub>4</sub> OH.....	1.74

It must be noted that in the above table the values are for normal solutions with platinum electrodes. If the solutions be more concentrated the decomposition potentials are lower. If electrodes other than platinum are used the values also vary for reasons cited below.

It should be noted that the decomposition values for the oxygen acids and bases are nearly the same. This is because the products of electrolysis are the same, *viz.*, hydrogen and oxygen, and hence we are really obtaining the decomposition potential of water, about 1.67 volts.

According to the solution tension hypothesis we can consider the decomposition potential of an electrolyte to be made up of two factors — the potential required to force cations to give up their electrical charges plus that required to force the anions to do likewise. This should then be the converse of the solution tension (p. 496) and have the same value as the electrode potentials. If hydrogen be taken as a standard, and we assume that it has zero solution tension, the solution tension of the hydroxyl ion of water should be  $1.67 - 0 = 1.67$ . In a similar way we can gain a knowledge of the **intensity of fixation** or **electrode potential** of elements or of radicals not directly determinable. A few of these are given in the following table which may be considered as an extension of the table of electrode potentials given on p. 497. The + sign indicates the impressed voltage needed



to prevent the material returning to the ionic form when the solution is of normal concentration.

I.....	+0.520	OH.....	+1.67
Br.....	+0.993	SO <sub>4</sub> .....	+1.9
O.....	+1.23	HSO <sub>4</sub> .....	+2.6
Cl.....	+1.31	NO <sub>3</sub> .....	+1.75

Two rather important points remain to be considered. When a solution of a salt is electrolyzed with deposition of the metal the decomposition potential must be increased as the dilution of the solution increases. This is strictly in accord with the solution tension hypothesis, since the more dilute the solution the greater the back electromotive force. The increase in order to secure a great dilution of the removed ion is not very great and may be calculated from the Nernst formula,  $\pi = \pi_0 + \frac{0.058}{n} \log \frac{1}{C}$ . (Cf. p. 498.)

When the products of the electrolysis are gaseous the decomposition potential varies with the different electrode material because the concentration of the gaseous material required for steady evolution varies not only with different electrodes but with the character of the surface. This variation as a rule increases the decomposition potential and the excess of potential required is known as **over-voltage**.

**Electrochemical Analysis.** — A very interesting application of these relations is utilized in making quantitative separations of the metals. This may be illustrated as follows: Suppose we have a mixture of the nitrates of cadmium, lead and silver in solution in water. If we subject this solution to electrolysis using a current of a potential of one volt, all the silver will deposit on the cathode (decomposition potential, 0.70 volt). When the silver is removed the potential is raised to about 1.6 volts and the electrolysis continued. The lead will now precipitate and when its deposition is complete the potential may be raised to above 2 volts when the cadmium also deposits. In a similar manner other mixtures of metal salts may be analyzed by proper selection of potentials.

The problem of electroanalysis is not quite so simple as it would appear from the above since it is also necessary to regulate the temperature and **current density** in order to secure coherent and adherent deposits. By current density is meant the quantity

of current in amperes per unit surface of cathode or anode. (For details see texts on electroanalysis.) This method of determination of metals is used especially for copper.

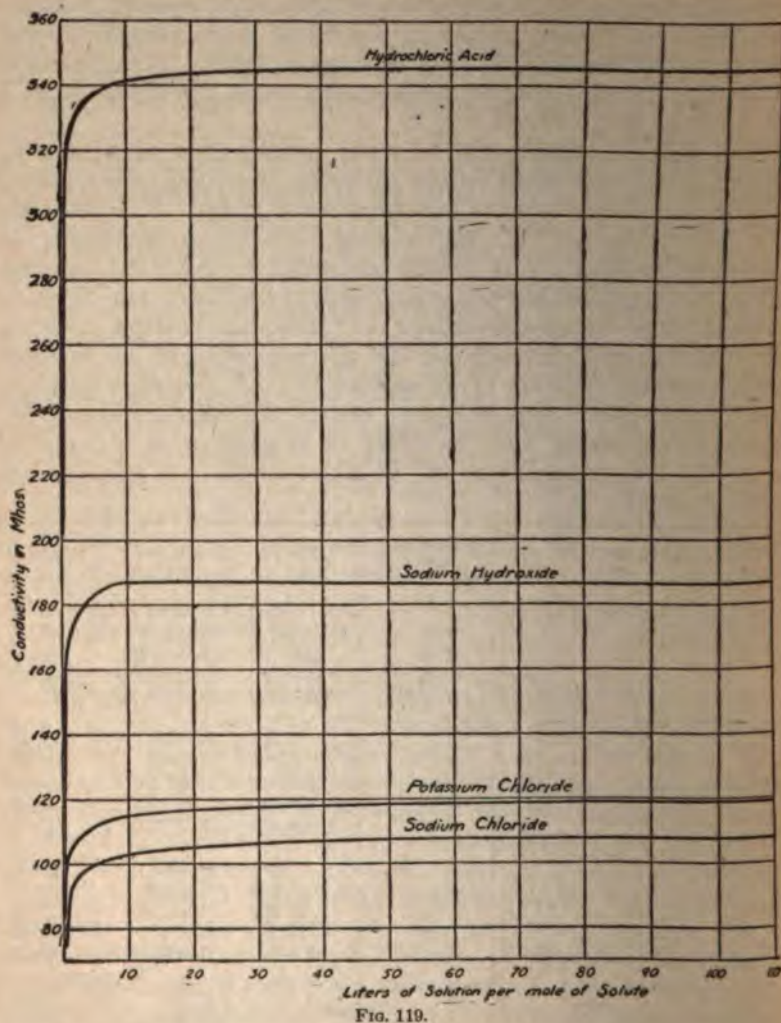
The modification of electroanalysis used for **metal purification** utilizes the same principles. In such cases the anode is a slab of impure metal, and the cathode a strip of pure metal. In the case of copper the copper ions deposit on the cathode and the anions migrate toward the anode, but so long as the potential is below the discharge potential they do not lose their charge, but instead the anode material ionizes and the electrolyte is kept at constant concentration. Since there is no polarization the current intensity is kept below 0.5 volt. Metals of solution tension less than  $+0.5$  do not therefore ionize at the anode, *e.g.*, silver, gold, etc., but collect at the bottom as anode mud. Those of greater solution tension, while they ionize, do not deposit on the cathode.

Another modification of large industrial importance is that of **electroplating**, particularly with silver and gold. Thus, for example, if a bath of silver potassium cyanide,  $KAg(CN)_2$ , is electrolyzed, the discharge potential of potassium ions being so much greater than that of silver ions, if the potential of the current be not too great, only the silver ion is deposited and if a base metal cathode is used it may be coated with silver and if the anode is silver the bath is kept at constant strength. The current potential must be at least 0.77 volt, not to cause the silver to deposit but to effect solution at the anode.

**Conductance (or Conductivity).** — The resistance of conductors of the first class is proportional to their length and inversely proportional to the area of their cross section. This is also true for conductors of the second class, electrolytes. The **specific resistance** of an electrolyte is therefore defined as the resistance in ohms (p. 170) of a column of the electrolyte 1 cm. in length and 1 cm. in cross section. It is usual for the chemist to consider the relative value of electrolytes according to the readiness with which they conduct the current, the conductance, rather than the difficulty, the resistance. The unit of conductance is then the reciprocal ohm, sometimes called 'mho. The **specific conductance**,  $K$ , is then the conductance of a column of the electrolyte 1 cm. in length and 1 cm. in cross section. Since pure liquids are as a rule practically non-conductors and the conductivity of solutions depends upon the solute present, it is more convenient



It will be observed that the specific conductance decreases with the dilution but that the equivalent conductance (in the



cases given the molar conductance is the same value) increases up to a certain point after which it remains nearly constant. This in terms of the ionization hypothesis is the point of maximum

ionization and is known as **infinite dilution**, since further dilution can have practically no effect on the conductance. The conductivity at infinite dilutions is usually represented by  $\lambda_{\infty}$  and that at any other dilution by  $\lambda_V$ . The effect of dilution on conductivity is also shown graphically in the figure (Fig. 119).

The chief value of conductance measurements for the chemist lies in the fact that through them we can most readily obtain reliable figures for the degree of ionization of electrolytes. If, as the hypothesis assumes, the conductance depends upon the number of ions present, the speed at which they move and upon their charge, we may assume without very great error (*cf.* p. 177) with a given electrolyte that at a fixed temperature the speed of the ions is not greatly affected by dilution (see hydration of ions, p. 511) and since their charge (p. 172) remains constant the variation in conductance at different dilutions is due to change in the number of ions. It follows therefore that the ratio  $\lambda_V/\lambda_{\infty}$  is the ratio of the number of ions present at a given dilution  $V$  to the maximum number which may be present at infinite dilution. If then  $\lambda_{\infty}$  can be determined for every electrolyte we have at hand the means of learning the degree of dissociation at any other lesser dilution. Unfortunately, while some electrolytes increase in conductance to a maximum at dilutions where the conductance is fairly readily determined, this is not always the case. Thus, for example, the conductance for acetic acid changes as follows:

$V$ in c.c. ....	100	1000	10,000	100,000	1,000,000	10,000,000
$\lambda$ .....	0.049	1.32	4.60	14.3	41	107

and is still increasing. At such great dilutions conductance measurements are unreliable and exact determinations of  $\lambda_{\infty}$  are therefore impossible. Fortunately there is a method of learning the value of  $\lambda_{\infty}$  by means of a knowledge of the migration ratios of the ions. For this reason, as well as because of some other important deductions, the topic will be briefly discussed.

**Migration of Ions.** — Since electrolysis of an electrolyte causes the deposition of equivalent amounts of positive and negative ions it might be inferred that at least all univalent ions move at the same speed. That this is not the case was inferred by Hittorf (1859) as the result of his study of the changes of concentration around electrodes during electrolysis long before the hypothesis of



ionization was reached. It will not be necessary in this connection to detail his method of determination of relative ratios since by modifications of an experiment first suggested by Sir Oliver Lodge not alone the fact of different rates can be shown visually, but the actual rate may be shown. See Fig. 120. The U tube is filled with a solution of sodium chloride which contains sufficient agar-agar, or gelatine, so that when cooled it solidifies. One limb of the tube is then filled partially with a similar solution containing also phenolphthalein which is colorless, and the other with the

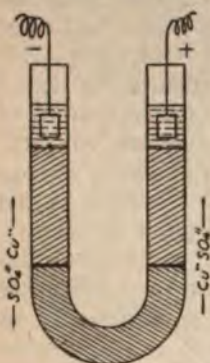


FIG. 120.

same solution to which a few drops of potassium hydroxide solution have been added. Into the remainder of the tube on one side is poured a mixture of cupric chloride and hydrochloric acid. Into the other side is poured potassium hydroxide. The whole is placed in ice water to prevent melting of the agar-agar when the current is passed. When a cathode from a current source is introduced into the alkaline side of the tube and an anode into the acid side electrolysis begins with migration of hydrogen and of copper toward the cathode and of hydroxyl toward the anode. The rate may be observed by change of color of the agar-

agar. The relative rates of the ions above indicated are approximately as 10 for hydrogen to 4 for hydroxyl to 1 for copper. There are various means by which these rates may be determined and the following table contains the absolute velocities of a few ions at 18°, when the potential difference is one volt per centimeter distance of the electrodes, in centimeters per second.

#### Absolute Ionic Velocities

H <sup>+</sup> .....	0.00320	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> .....	0.00069
K <sup>+</sup> .....	0.00066	Cl <sup>-</sup> .....	0.00064
NH <sub>4</sub> <sup>+</sup> .....	0.00066	ClO <sub>3</sub> <sup>-</sup> .....	0.00057
Na <sup>+</sup> .....	0.00045	NO <sub>3</sub> <sup>-</sup> .....	0.00064
Li <sup>+</sup> .....	0.00036	OH <sup>-</sup> .....	0.00181
Ag <sup>+</sup> .....	0.00057	SO <sub>4</sub> <sup>2-</sup> .....	0.00071
Cu <sup>2+</sup> .....	0.00031		

It would appear that at infinite dilution the conductance of a salt  $\lambda_{\infty}$  can be considered as made up of two factors, the conductivity of the anion,  $\lambda_a$ , and of the cation,  $\lambda_c$ , i.e.,  $\lambda_{\infty} = \lambda_a + \lambda_c$ .

From the data collected by Hittorf and subsequently by many others, the **relative** speed of the ions in a given electrolyte can be calculated by measuring the change in concentration around the electrodes and from this the values  $\lambda_a$  and  $\lambda_c$  in the above formula. (For details consult texts on electrochemistry.) A few of the values so obtained are given in the following table, for 18°.

Ionic Conductances at Infinite Dilution or Relative Mobilities of the Ions

H°.....	318.0	$\frac{1}{2}$ Mg°°.....	46.0
Li°.....	33.44	$\frac{1}{2}$ Ba°°.....	56.3
Na°.....	43.55	OH'.....	174.0
K°.....	64.67	Cl'.....	65.4
Rb°.....	67.6	Br'.....	67.3
Cs°.....	68.2	I'.....	66.4
NH <sub>4</sub> °.....	64.4	NO <sub>3</sub> '.....	61.8
Ag°.....	54.02	$\frac{1}{2}$ SO <sub>4</sub> ''.....	68.7
$\frac{1}{2}$ Cu°°.....	51.0	$\frac{1}{2}$ CO <sub>3</sub> ''.....	70.0
$\frac{1}{2}$ Zn°°.....	45.6	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> '.....	34.55

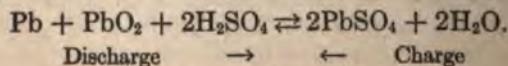
If the reasoning and measurements by which the above results are reached are correct it is only necessary to add the proper ionic conductances, called **mobilities**, of the ions, to get the value  $\lambda_\infty$  for any acid, base or salt where the mobilities are determined. This value for acetic acid is then  $318 + 34.55 = 352.55$ , and consequently the degree of dissociation of acetic acid is obtained. It is from data so determined that the degrees of dissociation given on p. 175 were obtained.

**Hydration of Ions.** — A striking feature of the preceding table is that the mobilities of the ions lithium, sodium, potassium, rubidium, and caesium are in the inverse order of what would be expected from the general experience that, when acted upon by the same force, lighter bodies move more rapidly. It was first suggested by Kohlrausch that each ion in moving through a solution carries with it an "atmosphere" of water and this has been converted by Washburn and others into the hydration of ions theory already mentioned (p. 511). According to this view the lithium ion, being hydrated to a greater extent, is really heavier than any of its family fellows and therefore moves more slowly. There is an abundance of collateral evidence from various sources that ions are hydrated, but up to the present time (1916) there is unfortunately not sufficient accurate data on which to base any general statements concerning the degree. In the face of this situation, coupled with the

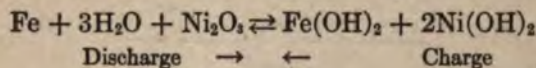


fact that the mobilities of the ions alter with change of concentration due to changes in viscosity of the solution and the further fact that ionization has a certain, though usually small, temperature coefficient, the simple relation  $\lambda_V/\lambda_\infty$  does not give accurate dissociation degrees. Taking into account certain of these factors, Noyes and Falk (Jour. Amer. Chem. Soc., Vol. 34, p. 456 (1912)) published tables of data which modify the dissociation values materially and bring them into closer accord with freezing point data (cf. p. 175 *et seq.*).

**Reversible Cells and Storage Batteries.**—Any electrolytic cell from which the products of electrolysis do not escape can in turn deliver current and so become a voltaic cell. Whether, and to what extent, a cell is reversible depends also on whether secondary changes take place when the ions are discharged, and upon the temperature coefficient of the cell. An example of a practically perfectly reversible cell is furnished by the Daniell cell in which, while operating as a voltaic cell, zinc is converted into zinc sulfate and the copper is deposited. If a current of slightly greater potential is passed through the cell in the reverse direction copper is converted to copper sulfate and zinc is deposited. Since in both cases there is but a slight temperature coefficient the mutual transformations are made at a sacrifice of but small energy loss and the reaction may be expressed  $\text{Zn} + \text{CuSO}_4 \rightleftharpoons \text{Cu} + \text{ZnSO}_4$ . Any such cell may therefore be used as a **storage battery**, in which electrical energy may be stored up as chemical energy for use when desired. The two cells most used practically are the lead battery called also the **Planté cell** or the **lead accumulator** and the nickel-iron-alkali cell, ordinarily called the Edison battery. The former consists of two lead electrodes, one of which is a plate covered with spongy lead and the other a lead framework or grooved plate in which the holes or grooves are filled with lead peroxide. The space between the plates is filled with sulfuric acid (sp. gr. 1.4). The cell is essentially then the system  $\text{Pb}-\text{H}_2\text{SO}_4 \text{ Aq.}-\text{PbO}_2$ . This cell delivers current at a potential of about 2 volts and in so doing both lead and lead peroxide are converted to lead sulfate. When the cell is being charged, the lead sulfate is converted at the cathode to lead and at the anode to lead peroxide, so the reaction may be written reversibly:



The efficiency of this cell is variously rated at from 76 to 88 per cent. The Edison cell is the system composed of a nickel-plated grid with pockets filled with finely divided iron for one electrode and a similar grid with pockets filled with nickel peroxide for the other. The cell is filled with a 20 per cent solution of potassium hydroxide. Its electromotive force is 1.2 volts. The efficiency of the cell is from 60 to 65 per cent but it has the advantage over the lead accumulator of being both lighter and less easily damaged by careless handling. The reactions in the Edison cell are probably



**Oxidation — Reduction Cells.**—The electromotive series of the metals is also the order of their oxidizability and therefore the electrode potential is a measure of the intensity factor of their affinities for oxygen. As was mentioned on p. 228, the terms "oxidation" and "reduction" have been extended to cover all phenomena in which a change of valence occurs whether oxygen is involved in the process or not. When, then, we place a strip of zinc in a copper solution we say that zinc is oxidized from  $\text{Zn}$  to  $\text{Zn}^{\circ\circ}$  and the copper reduced from  $\text{Cu}^{\circ\circ}$  to  $\text{Cu}$ . Similarly, when chlorine ions are discharged from an electrolyte the change is an oxidation, *i.e.*, the valence is changed from  $-1$  to  $0$ . In general, oxidation may be defined as a decrease of negative valence or an increase of positive valence and conversely, reduction. In terms of ions this relation is that oxidation is change of ionic charge in the positive direction and in terms of the electron hypothesis (*q.v.*) oxidation corresponds to the loss of negative electrons. Change of valence may, however, occur without complete discharge of any ion. Thus cupric chloride may be reduced to cuprous chloride, the change being from  $\text{Cu}^{\circ\circ}$  to  $\text{Cu}^{\circ}$ , and potassium ferrocyanide may be oxidized to potassium ferricyanide,  $\text{Fe}(\text{CN})_6^{\text{'''}}$  to  $\text{Fe}(\text{CN})_6^{\text{''}}$ . It is usual to classify reagents according to whether their general tendency is to effect oxidation or the converse. The most usual oxidizing agents are, oxygen, ozone, the peroxides, the halogens, permanganic acid and the higher oxyacids in general, potassium ferricyanide, stannic chloride, and the higher oxides of the metals. These are reduced when acting as oxidizing agents. The most usual reducing agents are hydrogen, metallic hydrides, the hydrides of sulfur, of iodine, and of phosphorus, etc., the active metals, the lower oxyacids, etc.



A very interesting example of continuity is furnished by the relation of these substances to each other with respect to their behavior in a type of cell known as **oxidation and reduction cells**. One of these may be illustrated as follows: Prepare a salt solution in two beakers connected with a salt bridge as indicated in the figure (Fig. 121). Connect the two solutions in the beakers by means of platinum electrodes with a sensitive **voltmeter**. When all is ready place in one beaker some ferric chloride and into the other pass hydrogen sulfide. A current flow is indicated in the

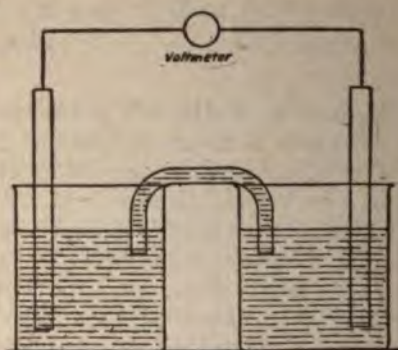


FIG. 121.

voltmeter and the ferric chloride is reduced to ferrous chloride and the hydrogen sulfide is oxidized to sulfur. This is sometimes called **chemical action at a distance**. The electromotive force produced by such a cell is a measure of the intensity of the chemical reaction. A large number of cells of this type have been investigated, especially by Bancroft (*Zeit. f. Phys. Chem.*, Vol. 10, p. 387), and by Neuman (*Zeit. f. Phys. Chem.*, Vol. 14, p. 193) and the following table represents a series of substances with their potentials such that the algebraic difference of the potentials represents the potential of a cell made up of any two of the compounds in solution. It should be observed that any one substance acts as a reducing agent upon any substance which follows it with an intensity measured by the differences in potential. Copper chloride is arbitrarily chosen as zero. It will be seen that the terms "oxidizing" and "reducing" substance are purely relative and any substance may be oxidizing with reference to some other. The use of the electric current for oxidizing or for reducing purposes in chemical manufacture is there-

fore not limited to the preparation of elements. The importance of this phase of electrochemistry is on the rapid increase.

#### Oxidation and Reduction Series

SnCl <sub>2</sub> in alkaline solution.....	-0.861
SnS.....	-0.651
H <sub>2</sub> in acid solution.....	-0.311
K <sub>4</sub> Fe(CN) <sub>6</sub> in alkaline solution.....	-0.086
SnCl <sub>2</sub> in acid solution.....	-0.064
CuCl <sub>2</sub> .....	0.000
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .....	+0.016
Na <sub>2</sub> SO <sub>3</sub> .....	+0.023
FeSO <sub>4</sub> in neutral solution.....	+0.073
NaHSO <sub>3</sub> .....	+0.103
H <sub>2</sub> SO <sub>3</sub> .....	+0.158
FeSO <sub>4</sub> in acid solution.....	+0.234
I <sub>2</sub> in potassium iodide solution.....	+0.328
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	+0.502
FeCl <sub>3</sub> .....	+0.678
HNO <sub>3</sub> .....	+0.697
Br <sub>2</sub> in alkaline solution.....	+0.755
H <sub>2</sub> CrO <sub>4</sub> .....	+0.837
KIO <sub>3</sub> .....	+0.929
Cl <sub>2</sub> in acid solution.....	+1.106
KMnO <sub>4</sub> .....	+1.203

**Exercises.**—1. If a copper coulometer cathode has increased in weight 250 milligrams in 15 minutes, what is the average current strength expressed in amperes? If the potential of the cell furnishing the current is 1.1 volts, how much electrical energy has been consumed? If the current came from a Daniell cell how much zinc is consumed? Assume no heat transformation in the cell.

2. What should be the E.M.F. of a cell made up as a Daniell cell but consisting of Fe—FeSO<sub>4</sub>—CoSO<sub>4</sub>—Co, where the sulfate salts are of normal concentration?

3. What should be the voltage of a cell made up of the chain K—K<sub>2</sub>SO<sub>4</sub>—AuCl<sub>3</sub>—Au, as above? Why cannot such a cell have its voltage directly determined?

4. Why cannot a cell be made of a **mixture** of zinc sulfate and copper sulfate with zinc and copper electrodes and show the same voltage as the Daniell cell?

5. In order that a hydrogen electrode should have in fact by



the Nernst hypothesis zero potential, what should be the concentration of the hydrogen in the electrode?

6. What weight of zinc must be consumed every hour in order to produce a current of five amperes? What would be the E.M.F. of the current if the zinc were in a solution normal with respect to its ions and the other electrode were a normal hydrogen electrode?

7. If zinc and tin in intimate mixture are treated with dilute hydrochloric acid in quantity not quite sufficient to dissolve all the zinc, what will happen to the tin, and why?

8. If zinc sulfate solution is decomposed between platinum electrodes and oxygen is liberated at the anode, what should be the decomposition potential? If now a copper anode is substituted what changes occur in the process and what is the maximum of potential needed?

9. If a zinc-copper-nickel alloy were to be separated into its components by an electrolytic method how would you proceed and what voltages would be employed?

10. If a potassium salt is electrolyzed using mercury as a cathode, how does the behavior differ from that when platinum is the cathode? Why?

11. Calculate the degree of ionization of  $N/100$  KCl, NaCl, NaOH and HCl from the data on p. 507.

12. With the ionic mobility of acetate ions and hydrogen ions (p. 511), calculate the degrees of ionization of acetic acid from the data on p. 509. Also calculate the ionization constant for acetic acid.

## CHAPTER XXIX

### ALUMINIUM AND ITS FAMILY

THE members of Group III are, with the exception of boron (p. 377), distinctly metallic in character and in general increase in basic character with increase in atomic weight. The two sub-groups are: (A) Scandium, yttrium, lanthanum, neoytterbium, and possibly actinium; (B) aluminium, gallium, indium, gadolinium, and thallium. All are classed as rare metals except aluminium. The discussion will therefore be largely confined to the one element.

**Occurrence.** — Aluminium, the third element in order of quantity (p. 5), and also third in importance as a metal, occurs most abundantly in the form of complex silicates and as clay. Examples are **albite**,  $\text{NaAlSi}_3\text{O}_8$ ; **orthoclase**,  $\text{KAlSi}_3\text{O}_8$ ; **mica**,  $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$ ; **kaolin**,  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ , etc. Certain mineral forms are jewels, such as **turquoise**,  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$ ; **garnets** are  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ . **Rubies** and **sapphires** are the oxide colored by small amounts of impurities. **Corundum**,  $\text{Al}_2\text{O}_3$ , is the oxide and in hardness ranks next to the diamond among minerals and has long been used as an abrasive, especially in the powdered or granulated form, known as emery. **Cryolite**,  $\text{Na}_3\text{AlF}_6$ , is a not uncommon mineral and is used to some extent for the manufacture of soda and also as the solvent for the aluminium compounds used as ores. The latter are for the most part **bauxite**, a more or less clearly defined compound of the type  $\text{Al}_2\text{O}_3(\text{OH})_4$ , and **alunite**,  $\text{K}(\text{AlO})_3(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ .

**History.** — The name "aluminium" was applied by the Romans to substances with a bitter taste, and the "alums" were early recognized as compounds containing a so-called earthy metal. Subsequent to Davy's work on the isolation of sodium and potassium many unsuccessful attempts were made to isolate the metal from alumina, i.e., the oxide. In 1827, Wöhler succeeded in obtaining the metal by fusion of aluminium chloride with potas-



sium, but even in 1855 the element was still worth about \$300 a pound. By 1855 the metal was prepared in various ways and by the time of Napoleon III was available in sufficient quantities so that extensive experiments were made by the French government with plans to utilize it for coinage and for military equipment. In 1854, Bunsen prepared it by electrolysis but not until after 1886, when C. M. Hall, a young graduate student at Oberlin, Ohio, discovered the method of electrolysis now used, was aluminium available at low enough prices to render it of general application.

**Preparation.** — Hall's process (Fig. 122) consisted in the electrolysis of oxides of aluminium dissolved in a bath of molten cryolite. This process, modified by details as to construction, is practically the only one used at present. The resistance of the electrolyte gives rise to the needed heat for keeping the mass liquid and the molten aluminium is deposited upon the bottom of the iron vessel in which the bath is held. The metal being tapped from the bottom and slag from the top, the process is continuous. The use of

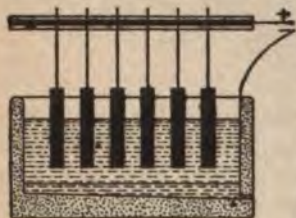
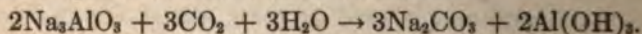


Fig. 122.

clays as a source of aluminium has not been found very practicable on a manufacturing scale. The ores of aluminium, *e.g.*, bauxite, are usually too impure for electrolysis and are purified by conversion to aluminates by fusion with alkalies and precipitation of the aluminium hydroxide with carbon dioxide.



The hydroxide is then ignited to form the oxide.

**Properties.** — Aluminium is a bluish-white metal of specific gravity 2.6. The metal is both ductile and malleable, especially at 50°, and can be rolled into sheets, or foil, or drawn out into wire, but is not of great tensile strength. At from 530–550° it is very brittle and can be powdered. The melting-point is 659° and its specific heat is 0.2356. It is a good conductor of both heat and electricity. The specific conductivity is at 0° 35.6 times that of mercury. It does not oxidize readily in air and in the presence of moisture seems to be protected by a superficial layer of oxide. This may or may not be true passivity (see p. 601).

It dissolves readily in hydrochloric acid or in aqua regia but only slowly in dilute nitric acid and not at all in the concentrated acid. When heated sufficiently it reacts with oxygen with a rapidity which results in the production of an intensely high temperature. The heat of combustion is 7140 cal. per gram. This reaction takes place even with oxides and sulfides of other metals and is utilized to produce rare and other metals (see Thermite). It unites with heated nitrogen to form nitrides. It also dissolves in alkali hydroxides to form aluminates with evolution of hydrogen. It does not dissolve in organic acids (passivity, see p. 601) but is dissolved by them in the presence of common salt. It is rapidly "rusted" by salt water. Its atomic weight is 27.1 as the mean value of various methods of determining its atomic weight. It is trivalent.

**Uses.** — The lightness of aluminium, together with its stability in the air, make it useful for a great range of purposes. It is used as a material for construction where small weight is desirable, as in the manufacture of airships, telescopes, etc. Cooking utensils and other household articles are now frequently made of aluminium and its use in this direction will increase as the cost of the substance lessens. It is, weight for weight, a better conductor than copper and its use in transmission lines will probably increase, though difficulties other than those involved in relative conductivity limit the utilization. These are both cost factors and tensile strength. Since it acquires the "passive" condition and becomes coated with non-conducting oxide, it is used in "rectifiers" of the alternating current and in lightning arresters for the protection of power plants, etc. (see passivity, p. 601). In powdered form mixed with various menstra it is used as a paint, witness the rural free delivery boxes. It is also used in large quantities in crucible steel casting as "medicine" to "quiet" the steel by absorbing the occluded oxygen and prevent "blow holes." Large quantities are used in the Goldschmidt process (*vide infra*) and in the manufacture of its alloys.

**The Goldschmidt Process (Thermite).** — If aluminium powder is mixed with the oxide of almost any metal and the mixture ignited by means of a mixture of magnesium and barium peroxide, the heat of combustion together with the reducing power of aluminium, converts the oxide to the molten metal, which col-



lects as a regulus in the bottom of the crucible. From this it may be tapped into suitable molds (Fig. 123). The temperature of the ignited mass can reach even to  $3500^{\circ}$ . This method of preparing metals is suitable for use with rare metal oxides; for

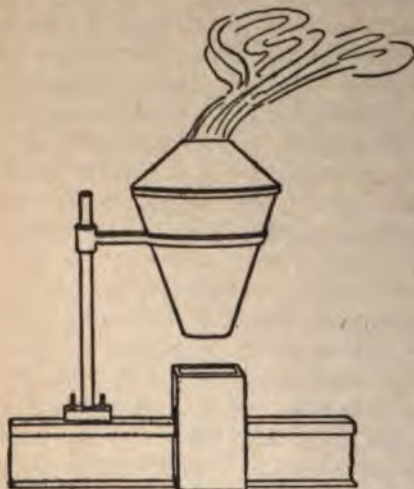


FIG. 123.

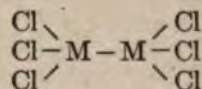
welding rails in street railway constructions; for repairing ships' propellers, etc. The suitable mixture for such purposes is prepared and sold as various kinds of "thermite." It is said that 175,000 pounds of thermite were used to repair the battleships sunk by the Japanese in the harbor at Port Arthur in the Russo-Japanese war. Thermite is also supposed to have been used as the chief compound of the incendiary bombs dropped by Zeppelins on London and other cities during the great war. A mixture of aluminium and ammonium nitrate is said to

compose the charge in the great howitzer shells used so effectively by the Austrian guns at Maubeuge and elsewhere (see *Current Opinion*, Vol. 60, p. 104, February 1916).

**Alloys of Aluminium.** — The alloys of aluminium present some interesting features. Aluminium amalgam is capable of interacting with water at room temperature to produce aluminium hydroxide and hydrogen. This is a contrast with the behavior of most other amalgams in which the amalgamated metal is less, rather than more, active than in pure condition. The amalgam may be used as a reducing agent in neutral solutions. Aluminium bronzes are used for automobile castings, being both light and durable. The effect of small percentages of copper on aluminium is remarkable, 2-3 per cent giving an alloy of silver-like luster, while 85-90 per cent gives an alloy closely resembling gold in color. Its luster is permanent in the air. The latter is much used in construction of ornamental articles. Magnalium, an alloy of magnesium and aluminium, is very light and easily turned

in a lathe. It has a higher tensile strength than the metal and is extensively used in automobile and airship construction.

**Compounds. Halides.**—Aluminium forms only one series of compounds and in these the metal is always trivalent. Of the halides, the chloride is perhaps the most important. It can be made in anhydrous form by passing chlorine over the heated metal, or over a heated mixture of the oxide and carbon. It is readily volatilized and at relatively low temperatures has a density corresponding to the formula  $\text{Al}_2\text{Cl}_6$ , but at higher temperatures to  $\text{AlCl}_3$ . This is as is to be expected but the double formula for aluminium chloride,  $\text{Al}_2\text{Cl}_6$ , ferric chloride,  $\text{Fe}_2\text{Cl}_6$ , and chromium chloride,  $\text{Cr}_2\text{Cl}_6$ , caused, for a period, the classification of these metals as tetravalent, *i.e.*, these compounds were regarded as being of the structure:

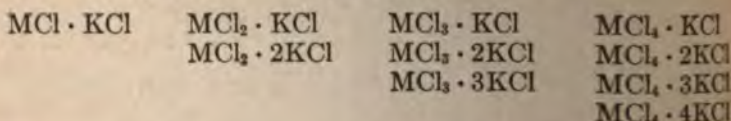


There seems to be no particular value in this conception in view of the general tendency to regard as the valence of an element the value shown in the simplest forms of its compounds. The anhydrous chloride is used in many organic reactions as a "catalyzer" (*e.g.*, Friedel and Craft's reaction). It cannot be obtained from a solution of aluminium chloride, for while the latter may be caused to crystallize as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , it is hydrolyzed by the water of crystallization when the attempt is made to drive it off, giving aluminium oxide and hydrochloric acid. Aluminium halides show a special tendency to form double halides with alkali halides, one of the most notable of which occurs in nature in considerable amounts, *viz.*, cryolite,  $\text{Na}_3\text{AlF}_6$ . A compound closely resembling this substance can be prepared artificially by treating aluminium hydroxide with an excess of hydrofluoric acid and this in turn with potassium acetate. The salt formed is probably  $\text{KH}_2\text{AlF}_6$ , which, if added to a solution of sodium salt, gives a precipitate. This reaction may be used as a qualitative test for sodium.

**Remsen's Double Halide Hypothesis.**—The halides of aluminium form a long series of double salts with the halides of the

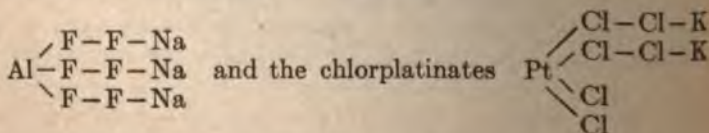


alkali metals. Remsen's view of the composition (*cf.* double halides) has been referred to and it is in place to present it formally here. Generally these double salts correspond in composition to the oxygen salts in which the oxygen is replaced by two halogen atoms. Thus potassium aluminium chloride,  $K_3AlCl_6$ , is analogous to  $K_3AlO_3$ , potassium aluminate. Antimony chloride and potassium chloride form  $K_3SbCl_6$ , which corresponds to potassium antimonite,  $K_3SbO_3$ . In some cases double halides exist when the corresponding oxygen compound is not known. According to Remsen a "careful study of the double chlorides, and the similar compounds of fluorine, bromine and iodine, shows that the chlorides of sodium, potassium, etc., combine with most other chlorides to form double salts and that the number of molecules of the alkali chloride which combine with another chloride is limited by the number of chlorine atoms contained in the other chloride." Thus, a chloride of the formula  $MCl_2$  may form  $MCl_2 \cdot KCl$  or  $MCl_2 \cdot 2KCl$ , or in general we may have:



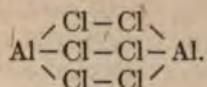
These may also be written as ordinary formulæ, for example,  $K_3MCl_6$ ,  $K_4MCl_8$ , etc.

As a usual thing these double halides are dissociated in solution so that the solutions show the reactions of both metal ions, but in some cases the compounds are sufficiently stable so that the free acids can be obtained. This is apparently the case with the so-called chlorplatonic acid,  $H_2PtCl_6$ . The formation of these compounds explains the increased solubility of insoluble halides in strong hydrochloric acid. Remsen's view of the structure of these halides is that the halogen atoms are at least bivalent and the structure is as illustrated by cryolite,



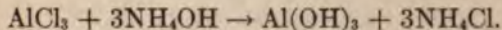
It is possible therefore that the reason for the double vapor density

of the chlorides of aluminium, iron and chromium, is due to the formation of these complexes, *e.g.*,



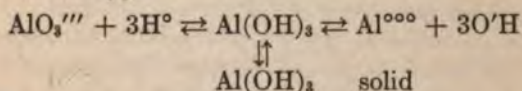
There is considerable evidence from conductivity measurements and otherwise that these complexes even exist with such salts as mercuric chloride, and that we have the systems  $\text{HgHgCl}_4 \rightleftharpoons 2\text{HgCl}_2$  and  $\text{BaBaCl}_4 \rightleftharpoons 2\text{BaCl}_2$  just as we have certainly the double cyanides  $\text{KAg}(\text{CN})_2$ , etc. It is probable also that all double salts can be accounted for by similar valence relations. (See also Werner's hypothesis.)

**Oxides and Hydroxides of Aluminium.** — When aluminium salts are treated with ammonium hydroxide the hydroxide is precipitated:



↓

This substance is amphoteric. It dissolves readily in acids, forming aluminium salts and in strong bases forming aluminates. It is fairly insoluble but its behavior toward solutions of reagents lead us to regard it in the presence of water as offering an equilibrium system of the type:



When heated the hydroxide apparently decomposes first into the meta-aluminic form:  $\text{Al}(\text{OH})_3 \rightarrow \text{Al}-\text{O}-\text{OH} + \text{H}_2\text{O}$ , compounds of which are very numerous in nature, forming the important group of minerals known as "spinel" (from *spinel*, the magnesium salt  $\text{Mg}(\text{AlO}_2)_2$ ). Other compounds of this type have been mentioned elsewhere, *franklinite*,  $\text{Zn}(\text{FeO}_2)_2$ , *chromite*,  $\text{Fe}(\text{CrO}_2)_2$ , etc. The complete dehydration of the hydroxide gives the oxide  $\text{Al}_2\text{O}_3$ , which, if heated to a high temperature, becomes practically insoluble in acids or bases. The oxide in this form is considered as an allotropic form and it also occurs in nature as *corundum* and *emery*. When the oxide is heated by the oxyhydrogen blowpipe to about  $1900^\circ$ , it melts and if cooled slowly forms a vitreous mass which may be cut into jewel-like forms known as white sapphires.



Its hardness is only exceeded by the diamond and carborundum. If colored with small quantities of oxides of chromium the green emerald of nature and the blood-red ruby may be made artificially. If the impure oxide is melted in an electric furnace a very refractory material, known as *alundum*, is prepared in the form of tubes, crucibles, etc. It is a very useful type of laboratory material. Aluminium hydroxide is much used as a mordant (*q.v.*). It is also used as a coagulant of finely suspended materials (much as white of egg is used in clearing coffee) so that the whole mass settles out of solution. This application is made in water purification and other filtrations.

**Aluminium Sulfate and the Alums.** — If the hydroxide or silicates of aluminium are digested with sulfuric acid the sulfate is prepared. It crystallizes from aqueous solution with 18 molecules of water,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . The solution is acid in reaction. It is used as a mordant and in sizing of paper. Paper is "sized" for the purpose of preventing the spread of ink. This is accomplished by distributing through the paper an insoluble material which is not wet in contact with water. With cheaper grades of paper this is accomplished by mixing a resinous soap with the paper. This is essentially a sodium resinate, which when treated with aluminium sulfate solution forms aluminium resinate and sodium sulfate. The resinate, being the salt of a very weak acid and base, is hydrolyzed to rosin and aluminium hydroxide. The effect is to distribute the rosin in finely divided form through the pulp so that when the paper is passed through the hot rolls, at the last stage of paper making, the resin is melted and a thin layer of resin is left on the paper after it is cooled. For certain grades of paper other sizing is used and for blotting and other "bibulous" papers no sizing at all is used.

When aluminium sulfate solution is mixed with potassium sulfate and crystallized, beautiful octahedral crystals are formed which contain the factors  $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , in the proportions indicated. This is ordinarily written  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and known as alum. It is a very anciently known compound. It is found in mineral form in Italy, Utah, and elsewhere as alum stone or alunite,  $\text{K}(\text{AlO})_3(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ . From this the alum can be obtained by calcination and subsequent leaching. It has for many centuries found application as a mordant.  $\Delta$  Alum is a type of a large group of isomorphous substances called "alums." They are represented

usually by the general formula  $M'M''(SO_4)_2 \cdot 12H_2O$ , where  $M'$  may be either potassium, rubidium, caesium, ammonium, silver or thallium. Sodium alum loses its water of crystallization readily and is hence difficult to prepare. The lithium alum appears not to have been prepared. The  $M''$  may be either aluminium, chromium, ferric iron, or trivalent manganese. It is even possible to prepare alums using selenic in lieu of sulfuric acid. These substances furnish a most remarkable series of compounds crystallizing in the same system, and in general such crystals as are capable of growing when placed in saturated solutions of any other of the group. Of course, the deposited material differs in composition from the original crystal and may differ in color, but the structural form remains the same. Such groups are known as isomorphous groups, and it was assumed by Mitscherlich in 1817 that in such cases the same number of atoms combined in the same manner to produce the same crystalline form, the form being independent of the nature of the atoms, but determined solely by their number and mode of combination. This hypothesis, known improperly as the Law of Mitscherlich, was used by Berzelius in selecting the number to be used as atomic weight. Its usefulness was great because in isomorphous groups, if the atomic weight of one element is known that of all elements capable of replacing it may be determined. In several cases the same element may appear in several isomorphous groups. Thus, iron appears in the "alums" and also in the "vitriols" (*q.v.*). Besides being used as a mordant, alum is used in dissociated form as burnt alum, as a water absorbent and astringent in surgery, and the crystalline substance is used to "whiten" flour and "crisp" pickles, etc. For a time the potassium and ammonium alums were used in the manufacture of baking powders (*q.v.*). Now all the so-called "alum" powders are made by using a mixture of sodium sulfate and aluminium sulfate, dissociated, of course, with sodium bicarbonate. This mixture is familiarly known as S.A.S. (sodium aluminium sulfate), or C.T.S. (cream of tartar substitute). The latter usually contains some primary calcium phosphate.

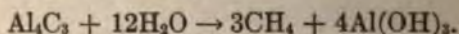
**Silicates of Aluminium.** — As already mentioned, these occur in great variety and in all sorts of degrees of purity in nature, and are used for many purposes, either as found or as modified by heat or otherwise. Thus, feldspars are used as glazes on pottery and porcelain; burned and more or less completely fused clay is used in



brick, terra cotta, porcelain, china, etc., etc. (See texts on industrial chemistry.) A very complex silicate containing sulfur occurs in nature as "lapis lazuli" and is of a beautiful blue color. It was formerly ground and used as a pigment. It is now made artificially, and much variation of color secured, by fusion of clay, charcoal, sodium carbonate and sulfur. Its composition varies somewhat and its structure is not known. It is much used as a pigment in wall paper, and otherwise.

**Other Compounds of Aluminium.** — Aluminium sulfide and carbonate cannot be made in the wet way because of the rapidity of their hydrolysis in water, but the carbonate evidently is formed by precipitation of aluminium salts by carbonates, as is very evident by the appearance of the precipitate and the change which occurs when, after a short interval, effervescence begins. Aluminium acetate can be crystallized from strong solutions but it also hydrolyzes completely in boiling solutions.

Aluminium carbide,  $\text{Al}_4\text{C}_3$ , made by Moissan by heating carbon and aluminium in an electric furnace, has a special interest because by hydrolysis it forms methane,



Methane is the chief constituent of natural gas and hence, just as acetylene is produced from water and calcium carbide, it may be that natural gas and at least certain deposits of petroleum, a mixture of homologues of methane, are so formed. This is Mendeleeff's theory of the origin of petroleum, and while probably not of general application is interesting as a possibility.

**Hydrate Theory.** — In 1886, Mendeleeff (Ber. d. Chem. Ges., 19, p. 379) suggested that certain substances when dissolved in water unite with water to form definite hydrates which exist as such in solution and in some instances these hydrates may be separated in solid condition giving crystalline hydrates. In other cases such hydrates are unstable and exist only in solution. In 1900, Jones and Chambers from a study of the freezing point lowering of concentrated solutions of certain chlorides, reached the conclusion that the hydration is the normal result of solution and is the factor which accounts for the failure of concentrated solutions to give the so-called normal freezing point lowering demanded by van't Hoff's theory (*cf.*, p. 164). The abnormal

great freezing point lowerings are, however, to be accounted for if any considerable proportion of the water present is associated with the solute, thus making the concentration greater than appears from the amount of solvent used. Indeed, it seems from the work of Jones and his co-workers that the degree of hydration is sometimes very great. Thus, one molecule of calcium chloride is calculated to be united with 13 molecules of water when the molar concentration is 3.2 and with 29 molecules at a concentration of 0.1. Aluminium chloride has a range of hydration from 16 to 38 at various concentrations. In 1904 this conception was extended to all solvents and the general conclusion reached that the power of dissolved substances to combine with more or less of the solvent is general. (A résumé of the solvate theory is found in the *Am. Chem. Jour.*, Vol. 41, p. 19.)

**The Rare Metals.**—The term *rare earth* is used to describe a group of basic oxides of elements which resemble one another very closely. They include the remaining members of Group III, many members of Group IV and certain other elements the places of which in the periodic system are uncertain. Indeed Crooks says of them, "The rare earths form a group to themselves: chemically they are so much alike that it taxes the utmost skill of the chemist to effect even a partial separation and their history is so obscure that we do not yet know the number of them." In the broadest sense the list of rare earths includes three sub-groups, the yttrium group, the cerium group and the thorium group. The last, being more distinctly tetravalent than the others, are sometimes not included in the designation. Besides the elements of sufficiently established identity to find places in the atomic weight tables and which are at least mentioned in the following discussion, there are several which have been announced but not yet certified by the international committee, and several others which have had their claim for inclusion disallowed. Among the latter may be mentioned, "phillippium," "carolinium," and "noria," and "jargonium" oxides of supposed elements.

**Occurrence.**—The materials containing these earths in traces sufficient for spectroscopic detection are fairly widely distributed, but in any appreciable quantities are of very limited occurrence. They are never found alone, and indeed the ores are usually complex mixtures. For example, from *gadolinite* have been separated at least sixteen elements. The more important ores contain the rare elements in varying proportions and usually a preponderance of



one of the sub-groups. Some of these are: **Cerite**, a basic silicate, the original source of the cerium group, is found chiefly in Sweden and contains 60 to 70 per cent of the cerite earths and a small percentage of yttrium earths, besides iron and calcium; **allanite** or **orthite** is widely distributed in small amounts in granites and like minerals. It is a cerite-aluminium silicate containing cerite earths (12-15 per cent), yttrium earths (5-8 per cent), along with several of the ordinary metals; **monazite**, the chief source of cerium as well as of several other elements, usually is found as a yellow sand, and is a cerium earth phosphate containing considerable quantities of thorium and of the yttrium group. It is found chiefly in the river sands of North and South Carolina and in Brazil; **gadolinite**, the original source of yttrium, is a basic silicate containing 40 to 48 per cent yttrium earths and 5 to 10 per cent cerite earths. Besides these specifically rare earth minerals the uranium minerals (*q.v.*) and the thorium and zirconium minerals also contain rare earths.

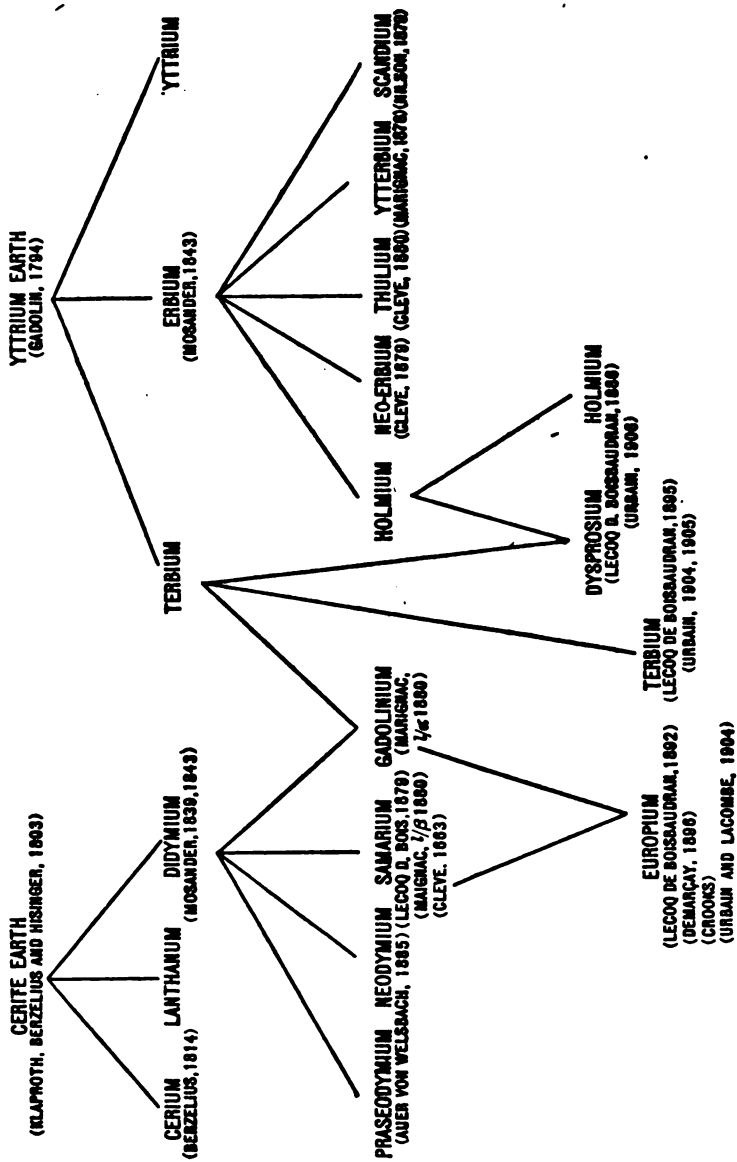
**History.**—In 1794, Gadolin discovered a new oxide in the mineral *gadolinite* and it was by Ekeberg named yttrium from the mines of Ytterby, where it was discovered. In 1803, Klaproth and also Berzelius discovered a new oxide in the mineral known as cerite. This was called cerium. In both cases the discoverers had a mixture of oxides which have subsequently been shown to be separable. Without going into details of the minerals used as starting points nor with the various and extremely numerous investigations the ultimate results may be presented in the form of a table taken from Abegg, Vol. III, pt. 1, p. 140.

**Preparation.**—The rare earths are separated from the complex minerals which contain them by digestion with concentrated sulfuric acid, and, after dilution, the clear filtrate is treated with hydrogen sulfide to remove the metals whose sulfides are insoluble, such as copper, bismuth, molybdenum, etc. The filtrate from the sulfides is treated with oxalic acid which precipitates the insoluble oxalates; or it may be treated with ammonium hydroxide to precipitate the hydroxides. In either case the precipitated compounds are ignited to render alumina and silica insoluble and the ignited oxides are dissolved in acids. The oxalates may now be reprecipitated and the precipitate roughly separated into three groups according to the relative solubility of the double sulfate with potassium. The double sulfates of the following are insoluble, scandium, lanthanum, cerium, praseodymium, neodymium, samarium; slightly soluble, europium, gadolinium and terbium; very soluble, yttrium, dysprosium, erbium, thulium, holmium, neoytterbium, and lutecium.

The further separation of these fractions is a very difficult and tedious operation which depends on either the fractional precipitation of the solutions with bases or on the fractional decomposition of the solid nitrates by heat. After successive treatments by one or both of these methods the fractions are further separated by taking advantage of small differences of solubility of various salts, and in some instances the fractionation has to be repeated hundreds of times. Even so it remains somewhat doubtful if in any instance complete



## CHART OF THE DISCOVERY OF THE RARE EARTHS





separation into individual elements has been reached. The progress of the fractionation can be watched, *i.e.*, controlled, by atomic weight determination of successive fractions or by examination of the spectra of the fractions.

The elements themselves may be prepared, only with difficulty, from the chlorides by treatment with sodium or potassium, but by electrolysis of the melted chloride the elements can be readily prepared. The purity of the product will, of course, depend upon the purity of the chloride used.

**Properties.** — The rare earth metals are in general white or yellowish and are fairly stable in the air. They have, in general, the property of uniting at high temperature with hydrogen, nitrogen and with carbon. The carbides react with water to form a mixture of acetylene (*cf.* calcium carbide), methane (*cf.* aluminium carbide), and ethylene, and this behavior is part of the basis of Mendeleeff's view of the origin of petroleum. When heated, they, of course, burn and the heat of combustion is so great that a mixture of these metals is suggested as a fuel for use in the Goldschmidt process. The heat of formation of the mixed oxides from the "mixed metal" (40 per cent of cerium) is greater than that of aluminium oxide. The oxides are all basic, and, as the preparation of the elements would indicate, they resemble each other so closely that they form a series of compounds with closely related properties. The oxides and salts are in general colorless, though the compounds of cerium with higher valence are yellow or red, the salts of praseodymium are green and those of neodymium are amethyst. In general, the elements appear to be trivalent though unstable compounds of the tetravalent type are known for praseodymium and neodymium, and the ceric salts are fairly stable. The vapor densities of the salts are practically unknown. The atomic weights range from 44.1 for scandium to 174 for lutecium, and while some of the elements find ready and apparently definite location in the periodic system, yet from cerium (140.2) to lutecium, the properties are so similar that if the elements are placed in the otherwise vacant places in series 7, 8 and 9, there seems to be but little evidence of a relation of a periodic sort. Indeed, the periodic system in no way leads to the expectation of a series of elements of this sort. It is true, however, that the properties of these elements are not sufficiently defined to make very definite statements concerning them.

One suggestion is of special interest because of the recent "transmutation of elements," growing out of a study of radioactivity (*q.v.*). It is that of Crooks, who, in 1887, suggested that these elements are all modifications of one element and proposes to call the fractions **meta-elements**. The properties of the separate elements are, therefore, to be regarded as the mean of the properties of the meta-elements. This view is called by R. J. Meyer "fantastic," but is nevertheless a basis for the theory of inorganic evolution (*Chem. News*, 55, 183). (See also Prout's Hypothesis, and Lockyer and Crooks' *Protyle*.) (*Cf.* Chapter XXXVI.)

**Uses.** — These rare earth metals have of recent years come into prominence in a technical way by reason of the utilization of the oxides of cerium and thorium as components of the Welsbach mantle for gas burners. (*Cf.* Thorium.) This

utilization has made the other rare elements by-products so to speak, and it is to be expected that uses for them will be found. There will be no special discussion of the compounds of the rare earth metals and only brief mention of certain points concerning some of them as they find proper place in the following pages.

### SUB-GROUP A

#### Scandium, Yttrium, Lanthanum, and Ytterbium

**Scandium, Sc**, was first prepared in 1879 by Nilson from gadolinite and also from euxenite, which is a titanate of the yttrium and cerium earths. The rarity of the element is indicated by the fact that Nilson could obtain from 10 kilos of euxenite only 2 g. of scandia,  $\text{Sc}_2\text{O}_3$ . The element was shown by Mendeleeff (Berichte, 20, p. 282), to be the eka boron prophesied by him in 1871 and its place in the third group was thereby established. It is the least basic of the rare earths, but even its salts are but slightly hydrolyzed in water. It has the lowest atomic weight, 44.1, of any of the rare earth metals. It has, therefore, several properties which distinguish it from its fellows and there is some doubt that it should be so classified, in spite of its natural occurrence with them. The salts are all colorless and the sulfate, selenite, nitrate, and oxalate have been investigated. They find at present no technical applications.

**Yttrium, Yt**, the first discovered of the rare earths, by Gadolin, in 1794, has been frequently investigated and a long series of its salts have been prepared. It has also been prepared in the metallic condition. Neither it nor its salts have so far found technical application.

**Lanthanum, La**, discovered by Mosander in 1839, has had its atomic weight determined through at least twenty-two separate investigations, yet it is not certain that the material so described is elementary. It is the most positive of all the rare earths, its sulfate the least soluble, its oxide absorbs carbon dioxide from the air and reacts with water to form a somewhat soluble base. The metal reacts with water and liberates hydrogen. Indeed, in practically all respects it acts as if its place were in the second group of the periodic system. Yet its atomic weight is 139.0 and its valence apparently three. Since there is no vacant place in the second group, it is placed in the third group and we must frankly admit a defect in the periodic system. The metal and a long series of its salts have been prepared, yet it finds no technical application except that it is said to be one of the constituents of the alloy known as Auer metal and used for gas and cigar lighters. (Cf. cerium.)

**(Neo) Ytterbium, Yb**, prepared first in 1878 by Marignac, is by peculiar contrast with lanthanum, a much less strongly basic element. Its place in the third periodic group is somewhat doubtful. In 1906 the original ytterbium was separated into the parts known as neoytterbium by Welsbach and also by Urbain



(at. wt. 172) and lutecium (at. wt. 174). Neither of these elements nor any of their salts are as yet of any technical use.

### SUB-GROUP B

#### Gallium, Indium, Gadolinium, and Thallium

None of these elements belong to the rare earth group except gadolinium, and it is somewhat doubtful if it should belong here. They are, however, all rare elements. Indeed, while somewhat widely distributed, they have never been found, except in one case (*cf.* thallium), to an extent of more than 0.1 per cent in any mineral. They are, therefore, of but small technical importance and their discussion will be limited to a few points of scientific interest.

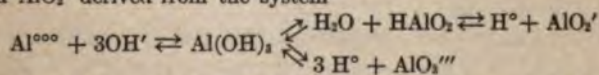
**Gallium, Ga**, was discovered by Le Coq de Boisbaudran in 1875. It appears frequently to accompany zinc blende though in extremely small and variable amounts. The material through the investigation of which it was discovered contained only about 0.002 per cent. The most characteristic property is the presence of two violet lines in its spectrum and the presence of these lines led to its discovery and isolation. The most interesting feature of gallium is the marvelous manner in which its properties correspond to the eka-aluminium prophesied by Mendeleeff. (*Cf.* p. 210.) The element is also remarkable as being the only metal other than mercury which is liquid at the ordinary temperature. While the melting point of the metal is  $30.2^{\circ}$  yet when cooled it "super cools," to a most remarkable extent and remains liquid at  $0^{\circ}$ . Ostwald suggests that the supercooling is due to the absence of particles of it in the air to act as "inoculating agents," to start crystallization, since the minutest particle of the solid causes immediate crystallization. The metal adheres readily to glass and forms an excellent mirror. These and other properties would render the metal very useful could it only be found in quantity. (The richest known sources are the zinc ores of the Cleveland district, England, which contain only 0.003 per cent.) Gallium forms two series of salts, gallous salts in which it is bivalent, and gallic salts in which it is trivalent.

**Indium, In**, was also discovered in zinc blende from Freiburg, in 1863, by Reich and Richter, which was being examined spectroscopically for thallium. The element shows a characteristic bright blue spectral line; hence the name, from indigo. It has never certainly been found in any minerals save zinc ores and in them it never exceeds 0.1 per cent. The element possesses a special interest because from its equivalent weight, about 38.2 and its supposed valence of 2, the atomic weight was supposed to be 76, but this atomic weight did not fit into the periodic system and Mendeleeff assumed the supposed atomic weight to be incorrect (1871). Bunsen (1871) found the specific heat to be 0.057 and therefore  $(0.057 \times 115 = 6.55)$  the atomic weight is more probably 115. It was also shown to form an alum isomorphous with the ordinary alum

and therefore to be trivalent. The vapor density of the chloride has been found to vary from 8.15 at 606° to 6.71 at 1048°. The assumption of Mendeleeff is therefore amply confirmed. The atomic weight is 114.8. While in general indium functions as a trivalent element and the trivalent compounds are the most stable, it also forms well-defined compounds of the univalent and also the bivalent type.

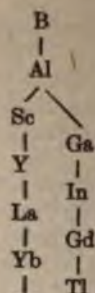
**Thallium, Tl**, discovered in 1861 by Crooks during the spectroscopic examination of the slimes from the lead chamber of a sulfuric acid factory. The most characteristic line was a green one and the name is derived from *θαλλός* = a green twig. Like indium and gallium, it is found only in very small amounts in any of the minerals in which it is present, except in the very rare mineral *crooksite* which though essentially a copper selenide contains from 16 to 18 per cent thallium. It is much more widespread than either of its fellows. Thallium as a metal has properties very similar to those of lead, though it is softer and has a lower melting point, 301°. Its specific gravity, 11.9, is between that of mercury and lead. Doubtless were it available in quantity it would find extensive uses. Its chemical behavior is strangely varied. It forms three series of compounds, the trivalent series corresponding, though not closely, to those of aluminium. The hydroxide,  $Tl(OH)_3$ , is red in color and is not soluble in ammonium sulfide (*cf.* antimony). The thallic salts are in general unstable. There are no salts in which the element is bivalent and the more stable series seems to be that in which the element is univalent and resembles in behavior univalent mercury and silver in that the chloride is insoluble in water, and the double cyanides are readily formed and are soluble in water. On the other hand, its hydroxide, carbonate, phosphate, sulfate and oxalate are soluble in water and resemble in behavior the corresponding salts of potassium. Indeed, an alum,  $TlAl(SO_4)_2 \cdot 18H_2O$ , has been formed.

**Family Relationships.** — The members of the family have such varied properties that it is difficult to formulate them in any general way. Boron is so distinctly an acid-forming element that it is always considered with the non-metals. Of the others only aluminium is sufficiently frequently encountered to render a discussion of analytical properties profitable. It indeed furnishes two types of ions but in both types the aluminium is trivalent, viz.:  $Al'''$  and  $AlO_2'''$  and  $AlO_2'$  derived from the system



Since aluminium hydroxide is a very weak base, and is also insoluble, the salts of aluminium are largely hydrolyzed in water and those with weak acids are completely hydrolyzed. Aluminium, therefore, belongs in the third analytical group, and is precipitated as an hydroxide by means of ammonium sulfide. It is distinguished from the similarly precipitated hydroxides of chromium and ferric iron by being soluble in strong bases, the alkali hydroxides. An attempt will be made to tabulate some of the chief properties of the elements of the group and it may be noted that the relationships are somewhat as are depicted by the following sketch:





Attention should be called to the vacant space in this group. This is probably occupied by one of the associated elements or decomposition products of radium (see Chap. XXXIII).

	Atomic weight.	Specific gravity.	Atomic volume.	Melting point.	Valence.
Boron.....	11.0	2.45	4.5	2200° to 2500°	3
Aluminium.....	27.1	2.7	10	658.7°	3
Scandium.....	44.1	.....	.....	.....	3
Gallium.....	69.9	5.9	11.8	30.2°	2, 3
Yttrium.....	89	.....	.....	.....	3
Indium.....	114.8	7.4	15.5	176°	1, 2, 3
Lanthanum.....	139	6.16	22.7	870°	3
Gadolinium.....	157.3	.....	.....	.....	3
Ytterbium.....	172	.....	.....	.....	3
Thallium.....	204.0	11.8	17.3	301°	1, 3

**Exercises.** — 1. What is the heat of formation of aluminium oxide? What oxides might be expected to be reduced by the Goldschmidt process?

2. If a cryolite bath containing bauxite in solution is operated at a tension of 5.5 volts and a current strength of 7500 amperes with a yield of 18 kilograms aluminium per hour, what is the percentage efficiency of the current and how much energy in joules is converted into heat or is otherwise ineffective?

3. If the heat of formation of  $\text{Al}_2\text{O}_3$  is 380,000 cal.; that of  $\text{Fe}_2\text{O}_3$  is 195,000; the specific heat of iron 0.11; the heat of fusion of iron 23,000 cal. per kilogram, the specific heat of aluminium oxide 0.217, what is the maximum temperature which could be reached by a thermite made of ferric oxide and aluminium in

equivalent quantities? Assume that no heat escapes by radiation or otherwise.

4. The specific conductivity of copper is to that of aluminium as about 2 : 1. What would be the respective diameters and weight of two wires, one of copper and one of aluminium, of equal conductivity? At the market value of the two metals, which is the cheaper conductor other things being equal?

5. If the tensile strength of copper is to that of aluminium as 40 to 20, how would this affect construction of heavy transmission wire? Why not substitute the alloy magnalium?

6. Why would a single gram of mercuric chloride placed in an aluminium vessel full of water make a hole in it?

7. In the aluminium rectifiers the alternating current passes between an aluminium electrode and one of copper. One phase of the current is stopped because aluminium as an anode becomes a non-conductor. What might be the type of construction of a lightning arrester and why?

8. On the basis of the data on p. 523, write the structural formulæ of chromite, franklinite, hausmannite and magnetite.

9. On the basis of Remsen's double halide theory formulate the equilibrium which exists in an aqueous solution of sodium aluminium chloride,  $\text{Na}_3\text{AlCl}_6$ . What happens when electrolysis begins? How does the situation change as electrolysis proceeds?

10. A solution of a ferric alum when treated with potassium sulfocyanide,  $\text{KCNS}$ , becomes blood red. This is taken to indicate the presence of ferric ions. A solution of potassium ferri-cyanide is not affected by the sulfocyanide. Why the difference? Express the relation by equilibrium formulæ.

11. Write the equations for the formation of carbon dioxide from  $\text{NaHCO}_3$ , and (a) cream of tartar, (b) sodium and aluminium sulfate, (c) primary calcium phosphate. When these combinations are used separately for biscuit making what residues remain in the biscuit?

12. If three baking-powders were made, one using cream of tartar, one sodium aluminium sulfate (anhydrous) and one primary calcium phosphate, each in equimolecular proportions, what would be the relative leavening power, i.e., the relative volume of carbon dioxide per unit weight?



## CHAPTER XXX

### THERMOCHEMISTRY

**THERMOCHEMISTRY** may be defined as the topic which deals with the transformations of chemical energy into heat, and the converse. Since practically every chemical change involves an energy change and the energy relation is at least as important as the change of mass, various phases of thermochemistry have already been discussed. It remains to correlate some of these and supplement them to a limited extent.

Chemical changes which evolve heat are called **exothermic** and since the relation is essentially the same whatever form of energy is involved, the term is extended usually to cover all energy evolution which takes place at the sacrifice of chemical energy. It should be recalled that exothermic reactions are either synthetic changes, decompositions, or exchanges. Exothermic **compounds** are, however, those **produced** with evolution of energy. **Endothermic** changes are the converse of exothermic changes. Since the quantity of energy change involved in different chemical changes of any one type, *e.g.*, synthetic changes, vary all the way from intensely exothermic to highly endothermic, it is to be expected that in a continuous series of such changes it were possible that chemical changes with zero energy change could occur and one such probable instance has been cited already (p. 293). Attention may also be called to the artificial character of our classifications, since in a very real sense all our previous discussions have involved thermochemistry and even this chapter will involve many other classes of phenomena. The exothermal and endothermal relations might be treated separately but in order to emphasize the above point of view they will be discussed together.

#### ***Factors of Heat Energy and Methods of Measurements.***

As with other types of energy, convenience is gained by division into two factors. The intensity factor, temperature, determines whether heat transfer will take place, and the quantity factor, which is a measure of the amount of energy transferred when a heat

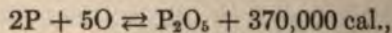
change takes place. The factors are measured by means of a variety of instruments the discussion of which is the province of a course in physics or of physical chemical measurements. Here no attempt will be made to go into detail but a general summary will be given.

Temperature is ordinarily expressed in degrees centigrade, Fahrenheit or Réaumur, and is measured either by the cubic expansion with change of temperature of suitable liquids such as mercury or alcohol; or of gases such as hydrogen which do not depart widely from Charles' law through wide ranges of temperature; or by the change in conductivity of certain metals with change of temperature; or by the differences of electromotive force produced at the junction of two dissimilar metals at different temperatures. For low temperature measurements either the hydrogen gas thermometer or the platinum, so-called "resistance" thermometer are used. At ordinary temperatures the mercury thermometer is employed, and where small variations are to be observed, it is usually of the Beckman type (p. 163). At high temperatures the platinum iridium couple is the usual device. (For details of construction and use see texts on physics.) The units of temperature have already been given (p. 77). Practically the only unit ever employed in science is the centigrade degree which is  $1/100$  of the difference of temperature of ice in equilibrium with water (freezing point) and water vapor at 76 cm. pressure in equilibrium with water (boiling point). The quantity factor of heat is measured by means of a large variety of instruments called by the general name of calorimeters. These range in size and complexity from the huge respiration calorimeters, which are essentially insulated living rooms, used for the study of the energy transformations which go on in the human body, to the small ice calorimeters, which measure the quantity of ice melted with a given heat change. The instruments used most generally by the chemist are the water calorimeter and the bomb calorimeter. (For details of the construction and operation of the bomb calorimeter consult any text on physical or physicochemical measurements. For a particularly efficient water calorimeter see Publication 38 of the Carnegie Institution, by Richards.) The unit quantity of heat is expressed either in calories or joules, preferably by the latter. The calorie has been defined (p. 43) and also its relation to the joule, but it is perhaps as well to restate the relation more accurately.



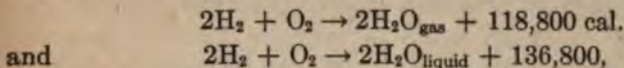
The unit of heat arbitrarily defined is the **calorie**, the amount of heat required to raise one gram of water from 15° to 16° centigrade. The most accurate determination of the mechanical equivalent of heat gives as the value 1 cal. = 42,660 gram centimeters (Callender and Barnes, Phil. Trans. 199, p. 149) and this value times the gravitation constant 980.5 gives  $4.183 \times 10^7$  ergs. The joule is defined as 10,000,000 ergs. 1 cal., therefore, is equal to 4.183 joules. It may be well also to call attention to the fact that frequently units 1000 times as great as these are employed and distinguished by differences in abbreviations employed. Thus 1 Cal. (kilo- or greater calorie) = 1000 cal. and 1 J. (kilo- or greater joule) = 1000 j. Occasionally also one encounters the use of the symbol *K* for a unit of heat equal to 100 cal. In this discussion, as throughout the book, the smaller units are employed. In technical work in the United States and the British Empire the commonly employed unit of heat is the British Thermal Unit (B.t.u.). (See p. 77.)

**Law of Lavoisier and La Place.** — What is sometimes called the fundamental law of thermochemistry is an obvious corollary of the law of conservation of energy. If a chemical reaction takes place with evolution of a certain quantity of heat exactly the same amount of heat is absorbed when by any means the reaction is reversed and the materials are brought back to their original condition. It is called the Law of Lavoisier and La Place because first stated by them in 1780, long before the law of conservation of energy was recognized as a universal law. The validity of this principle is recognized in the terms through which we express heat relations. Thus by the "heat of formation" of a compound we mean the energy in the form of heat (or other form of energy) which is either produced or absorbed when a formula weight in grams of the compound is produced or the reverse process takes place. Thus when in an equation we write, *e.g.*,



we mean that 370,000 calories are produced when 142 g. of phosphorus pentoxide are made and this same quantity is absorbed when this quantity of pentoxide is decomposed. In writing such equations we must bear in mind that any change of state also involves energy changes and consequently unless the state of

aggregation of materials is obvious it should be stated. The following conventions are used:



where the subscripts "gas" and "liquid" indicate the gaseous and liquid states respectively. Similarly, the fact that a substance is in aqueous solution is indicated by the subscript "aq."

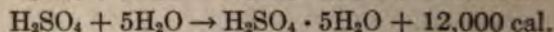
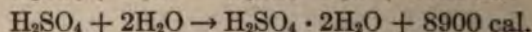
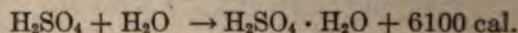
In writing energy equations such as the above it will be observed that the mass of the substances on the left side of the equations differs from the mass of the material on the right by quantities of energy. It would appear then that free hydrogen and oxygen differ from the mass represented by their symbols by a certain quantity of energy. This had led to a distinction between "simple substances" and elements. Thus Alexander Smith (see Smith's *Inorganic Chemistry*, p. 32) defines an element as a "kind of matter which never exists alone. It is always combined with more or less chemical energy and often with some other element or elements as well," but "a simple substance has independent existence and contains but one element combined with a certain quantity of energy." There is a certain value in this conception, since it enables us to express the relation between allotropic forms of elements. Thus red and yellow phosphorus differ, not in the mass, but in the energy content; and similarly for charcoal, graphite, and diamond; oxygen and ozone, etc. It is, however, impossible at present to state how much energy is associated with any elementary substance since not only does the energy appear in the free form (heat, light, etc.) only when two elements interact and therefore presumably comes in part from both, but the compounds formed also certainly still possess energy, since by further reaction with still other substances energy may be again liberated. Another viewpoint is presented in the footnote on p. 42.

**The Law of Constant Heat Summation.**—This law, as stated by Hess (see Ostwald's *Klassiker* No. 9, p. 11) is as follows: "If a compound is formed the heat of formation is the same whether formed directly or by several successive steps." This generalization is also a corollary of the law of conservation of energy but was developed before the more general truth was established and has some applications of special interest. The fundamental experiments

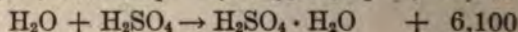
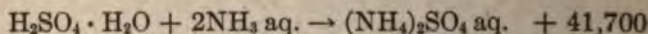
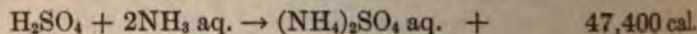


upon which Hess based his conclusion may be translated into our present forms of expression as follows:

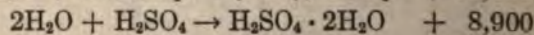
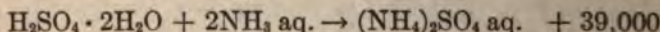
The heat of dilution of sulfuric acid with water was first determined. Thus:



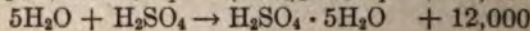
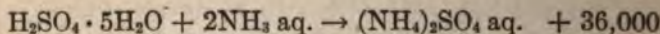
If now sulfuric acid and the hydrated acid are treated with ammonia in aqueous solution the following results obtain:



47,800 cal.



47,900 cal.



48,000 cal.

The variation of these values from constancy Hess rightly esteemed as due to experimental error and followed these initial experiments with a series of others designed to show the same relation. The specially useful feature of the law lies in that we can obtain knowledge of heat relations which cannot be directly determined. The case of carbon monoxide (p. 334) is an example. The heat of combustion of the monoxide to the dioxide and that of carbon to the dioxide can be directly determined. The difference ( $97,500 - 68,000 = 29,500$ ) is the heat of formation of the monoxide. (An extensive list of heats of formation is found in the Landolt, Bernstein, and Meyerhoffer Tables which are an essential to every departmental library.)

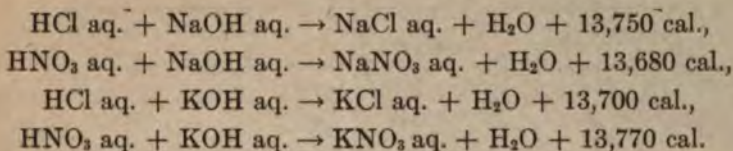
The fact that in general reactions take place more readily the greater the heat evolved and that in general the greater the heat of formation of a compound the more stable toward decomposition by use of temperature led to efforts to use thermochemical data to anticipate what reactions will take place under given

conditions. The first important effort in this direction is known as the principle of maximum work, announced by Berthelot (1879). "Every chemical process accomplished without the intervention of external energy tends to produce that substance, or system of substances, which evolves the most heat." While this statement is not correct in the form stated it is "a close approximation to a strictly valid law," but it precludes the possibility of spontaneous endothermic actions which we know certainly take place, *e.g.*, the evaporation of liquids and certain solids, the formation of acetylene and cyanogen at high temperatures, etc. The law would also lead one to expect all exothermic reactions to go to completion and this is contrary to the principle of reversibility as involved in the law of mass action (*q.v.*). We also find that the statement does not account for the initial "push" needed to initiate many reactions nor the effect of catalytic agents on the speed of reactions. It is for these reasons that the heat evolution of reactions, while an indication of affinity (the intensity factor of chemical energy), is not a measure of it. The heat of formation takes into account the total chemical energy converted into heat but not the quality of the change. However, through study of this "law" of Berthelot in an effort to bring it into accord with the facts, Le Chatelier was led to an immensely more comprehensive law which has already been utilized (p. 139). This law, or theorem, "Any system subjected to a stress tends to move in such a manner as to undo the stress," makes clear the reason so many exothermic reactions fail to go to completion since the rise of temperature produced by heat evolution would produce a stress which reversal of the reaction would tend to undo. It would also follow from this theorem that rise of temperature should tend to decompose all exothermic compounds and this is in accord with facts as we know them. It would also follow from the theorem that high temperatures should favor the formation of endothermic compounds. This we find also to be true (*vide* ozone, acetylene, cyanogen, nitric oxide, etc.). On the other hand, if the principle of maximum work represents an approximation to facts it is difficult to understand how any endothermic compound even if formed at high temperature could escape decomposition before reaching the ordinary temperature, since by its decomposition energy is liberated. Of course, we realize that any process, even exothermic processes, becomes slower with lowered temperature and consequently by sudden



cooling a temperature may be reached at which a given decomposition of an endothermic compound is so slow that practical permanency obtains. Thus, hydrogen peroxide decomposes slowly at ordinary temperature, though the change is exothermic. So also oxidation reactions at ordinary temperature may be very slow even when highly exothermic. There are, however, many cases such as the formation of nitric anhydride by distillation of nitric acid with phosphoric anhydride, the preparation of hypochlorous acid by distillation, etc., in which by further decomposition more energy would be evolved. The fact remains that such reactions are numerous and even where reactions proceed spontaneously they may go forward by steps and intermediate endothermic substances may be produced. (Ostwald's law of transformation by steps.) The facts formulated under the heads of the law of Lavoisier and Laplace, of constant heat summation and of maximum work, and even that of Le Chatelier still leave one unable to know in advance whether, when two or more substances are brought together, a reaction will take place and leave unanswered the question as to what causes chemical action.

**Laws of Thermoneutrality and Neutralization.** — In the same series of papers (see Ostwald's *Klassiker*, No. 9, 1841-1843) in which Hess announced the law of constant heat summation he also arrived at another statement, which, while not strictly valid, is the more interesting on that account. **In most cases if neutral salts are mixed when in dilute solution no thermal change takes place.** At first glance it would seem according to the law of mass action that a heat change must take place unless the heat of formation of both salts is the same. Thus, we might expect  $\text{NaNO}_3 + \text{KCl} \rightleftharpoons \text{KNO}_3 + \text{NaCl}$ . In the light of the ionization hypothesis, however, in dilute solution both salts are practically completely ionized as also are the products above indicated; hence we have only the ions  $\text{Na}^+ + \text{NO}_3^- + \text{K}^+ + \text{Cl}^-$ , both before and after mixing the solutions. Further, the exceptions to the validity of Hess' statement are also to be expected. These occur when one or both of the salts used are poor conductors of electricity and show other evidences of small ionization and in such cases reaction should take place. Another observation of Hess which likewise had to await the theory of ionization for explanation was the constant heat of neutralization of dilute acids by dilute bases, p. 179. A few examples follow:



This practical constancy finds explanation through ionization in that in dilute solution both acid and base and also the salt formed are completely ionized, while by neutralization water is formed and therefore  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + 13,700 \text{ cal.}$  When, however, weak acids are neutralized by strong bases the heat produced varies widely, from 13,700. The same is also true when weak bases react with strong acids. For example, formic acid and sodium hydroxide show a heat of neutralization of 13,400 cal. while formic acid and ammonium hydroxide give only 11,900 cal. A still more marked example is that of hydrocyanic acid and sodium hydroxide, where the heat of neutralization is only 2900 calories. The explanation of these variations is that the weak acids and bases being at the beginning but partially ionized the differences are due to energy absorbed during ionization. Since in the above case hydrocyanic acid is practically unionized in dilute solution (*cf.* p. 175) its heat of ionization is practically  $2900 - 13,700 = -10,800$  calories.

**Heat of Ionization.** — Since 13,700 calories of heat are liberated when water is produced from  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  and the heat of formation of water is 68,400 cal. it follows therefore that the heat of ionization of water is  $13,700 - 68,400 = -54,700 \text{ cal.}$  It was shown on p. 504 that but a very small expenditure of energy is required to ionize hydrogen and if we therefore take it as zero the heat of formation of hydroxyl ions from water may be considered as very close to  $-54,700 \text{ cal.}$  and it follows that to produce hydroxyl ions from hydrogen and oxygen involves the evolution of 54,700 cal. In a similar manner since the heat of formation of potassium hydroxide is 116,500 cal. the heat of formation of potassium ions is  $116,500 - 54,700 = 61,800 \text{ cal.}$

The following table shows the heat of formation of a few of the commoner ions as arrived at by this method. It should be recalled that these values represent the heat **evolved** when the ions are produced from the elements or **absorbed** when produced from their compounds.



Ion.	Heat of formation.	Ion.	Heat of formation.
H.....	0.0	Cu <sup>oo</sup> .....	-15,800
K.....	61,900	Cu <sup>o</sup> .....	-16,000
Na.....	57,500	Hg <sup>o</sup> .....	-19,800
Li.....	62,900	Ag.....	-25,000
NH <sub>4</sub> .....	32,800	Pb.....	500
Mg.....	109,000	Sn <sup>oo</sup> .....	3,300
Ca.....	109,000	Cl.....	39,300
Al.....	121,000	Br.....	28,200
Mn.....	50,200	I.....	13,100
Fe <sup>oo</sup> .....	22,200	SO <sub>4</sub> .....	214,000
Fe <sup>ooo</sup> .....	-9,300	NO <sub>3</sub> .....	49,000
Co.....	17,000	CO <sub>3</sub> .....	161,100
Ni.....	16,000	OH.....	54,700
Zn.....	35,100	NO <sub>2</sub> .....	27,000
Cd.....	18,400	SO <sub>2</sub> .....	151,300

The heat of formation of ions may be calculated from the difference of potential between a metal and a solution of its salts together with the temperature coefficient by means of the Gibbs-Helmholtz equation (see texts on physical chemistry) and also from the variation of the equilibrium constant with temperature (van't Hoff's Isochore Equation). The results agree fairly well with those above detailed but are by no means exactly the same. It may readily be that the discrepancies are due to the fact that when the heat of formation of substances is determined the values obtained are the resultant of at least the following factors; the heat of formation, the heat of ionization, the heat of hydration and the heat of conversion from gaseous or solid to the liquid state and the consequent changes in volume. Since the effect of these, and perhaps other factors, cannot be studied while the others remain constant the heats of ionization can be considered as only approximate.

**Heat of Solution.**—When either gases, liquids or solids dissolve in a liquid there is a certain heat effect which may be either positive or negative. This is known as the heat of solution and is expressed in calories per formula weight of solute. If not otherwise indicated it also indicates an amount of solvent such that further addition produces no measurable effect. Thus, the heat of solution of sulfuric acid is said to be 17,900 cal., meaning that this quantity of heat is evolved when 98 g. of acid are placed in an indefinitely great quantity of water. We know in this

instance and in many others that definite hydrates are formed, as for example with calcium oxide, hydrochloric acid, etc. Yet as water is gradually added there are no sharp changes in the rate of heat evolution such as one would expect from the formation of definite hydrates. The heat of solution of acids and of bases is usually positive but varies greatly. The heat of solution of salts is usually negative and may in part be due to the conversion from the solid to the "gaseous" state in which they exist in solution. A part of the heat which would otherwise be evolved in solution is undoubtedly absorbed by the ionization process. The following table presents the heat of solution in water of a few of the more common substances:

	Cal.		Cal.
HCl.....	20,300	NaCl.....	- 1,200
H <sub>2</sub> SO <sub>4</sub> .....	17,900	KCl.....	- 3,100
NH <sub>3</sub> .....	8,400	NH <sub>4</sub> Cl.....	- 4,000
HNO <sub>3</sub> .....	7,200	NH <sub>4</sub> NO <sub>3</sub> .....	- 6,400
H <sub>3</sub> PO <sub>4</sub> .....	2,700	KNO <sub>3</sub> .....	- 8,500
KOH.....	13,300	CaCl <sub>2</sub> .....	-17,400
NaOH.....	10,900	MgSO <sub>4</sub> .....	-20,300
Ca(OH) <sub>2</sub> .....	3,000		

**Temperature and Heat of Formation.**—The heat of formation of substances is not wholly independent of the temperature at which they are formed. Thus the heat of formation of hydriodic acid is at ordinary temperatures -6100 cal. while at 520° it is 2200 cal. (Zeit. für Phys. Chem., 29, p. 313). The explanation of this apparent anomaly is that the first value is the heat of reaction between solid iodine and gaseous hydrogen, while the second is between the partially dissociated gases. To convert iodine from a solid to the gaseous form requires the dissociation of the molecules and the absorption of heat. When the two gases are brought together at high temperature these losses do not have to be compensated. In determining, therefore, heats of reaction (including heats of combustion) changes of state have to be taken into account as well as changes of specific heat with change of temperature. To enter into a discussion of these matters would lead us too far into the special fields of physical, as well as of industrial, chemistry. They are, however, of considerable interest from both a theoretical and a technical standpoint.



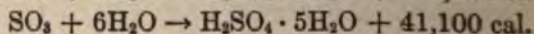
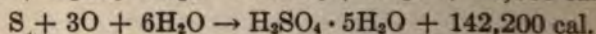
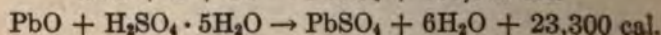
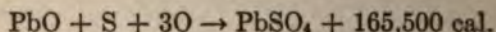
**Exercises.** — 1. If a calorimeter contains 3000 cc. of water, a quantity of iron weighing 500 g., and of glass weighing 50 g. (specific heat of the glass, 0.20), and of copper equal to 350 g., what is the quantity of heat represented when the calorimeter is raised 2° C. in temperature?

2. If the heat of formation of acetylene is -51,400 calories, of water 68,400 calories, of carbon dioxide 97,500 calories, how much heat is produced by burning a formula weight in grams of acetylene?

3. In order to determine the **temperature** produced in a perfectly isolated system when a formula weight of acetylene is burned, what factors must be known?

4. What is the heat of formation of zinc chloride in dilute solution if the reaction,  $\text{Zn} + 2\text{HCl aq.} = \text{ZnCl}_2 \text{ aq.} + \text{H}_2 + 34,400 \text{ cal.}$  and the heat of formation of  $\text{HCl aq.}$  is 78,600 calories?

5. Calculate the heat of formation of sulfur trioxide from the following data:



## CHAPTER XXXI

### THE FOURTH GROUP

THE elements of the fourth group are best considered in three sub-groups. The first two, carbon and silicon, being distinctly acid forming, have already been considered. (Chap. XIX-XXII.) The other members form two sub-groups which are metallic in character. As is usual acid character decreases with lower valency and with increased atomic weight. Sub-group *A* consists of titanium, zirconium, cerium, and thorium. All of these are usually classed as rare elements. Titanium is very abundant in nature but has as yet found but limited technical application. On the other hand, cerium and thorium compounds though sparingly found in nature are becoming increasingly familiar, due in part to their technical uses and in part to their very interesting chemical relations (*vide infra*). The elements of sub-group *B* are germanium, tin, and lead and while none are among the elements of more frequent occurrence, and germanium is very rare, yet the varied uses of tin and lead make them of frequent encounter. This sub-group will therefore be first discussed.

**Germanium.** — The chief interest attaching to germanium is the remarkable manner in which it conforms to the properties anticipated by Mendeleeff for *eka-silicon* and already detailed on p. 210. It is found in two very rare minerals *argyrodite* and *canfieldite*, both of which are silver sulfide minerals. The latter occurs in Bolivia and the former near Freiberg, Germany. The analysis of the *argyrodite* by Winkler gave in a given case, 17.04 per cent sulfur, 76.05 per cent silver and 0.13 per cent iron and zinc. The search for the remaining 6.78 per cent resulted in the discovery of the element. It proved to have the atomic weight 72.05 and to be both bivalent and tetravalent. The general properties of the bivalent salts are analogous to the corresponding compounds of silicon while those of the tetravalent type more closely resemble those of tin. There have so far developed no possible uses of the element or its compounds.

#### TIN

**Occurrence.** — Tin occurs native in very small quantities, but practically the only commercial source of the metal is *cassiterite*



or tinstone,  $\text{SnO}_2$ . Small quantities of it occur as "impurity" in other ores and minerals but these are not used as a source of the metal. Cassiterite occurs in masses in veins in the older crystalline rocks and is frequently found as water-worn pebbles in streams, hence the name "stream tin." The two greatest sources of tin are Cornwall and the Malay Peninsula. Smaller quantities are produced in various other localities. No tin is produced in the United States, though deposits of tin are reported from Alaska.

**History.** — Tin is one of the seven ancient metals and its sign  $\text{♄}$  was that assigned by astrologers to the planet Jupiter. The early history of tin is somewhat obscure. It is not certain whether the tin of the ancients came from India or from Cornwall, but it is certain that before the days of Cæsar's conquest of Britain, tin was mined in Cornwall. The Latin name for tin was "stannum," hence the names usually applied to tin salts and the symbol, Sn. The bitterness of tin alloys led to the alchemistic term "Devil's metal" for tin.

**Preparation.** — In the metallurgy of tin the ore is first concentrated by washing away the relatively lighter gangue. Frequently the ore is associated with iron oxide or sulfide, difficult to remove by concentration. Such ores are roasted and then separated by being passed through a strong magnetic field in such a manner that the fall of the oxide of iron is deflected by the field. This also effects separation from tungsten oxide if present. The concentrated ore is heated in a furnace with charcoal and the reduced metal drawn off and cast in ingots known as "block tin." The block tin may be purified by "liquation" or "poling." Tin is also recovered from "tinware" by treatment with chlorine.

**Properties.** — Tin is a lustrous white metal. It does not tarnish in the air. It is soft and readily worked but is not so soft as lead. It is both ductile and malleable. It is most malleable at about  $100^\circ$ , at higher temperatures it becomes brittle and at  $200^\circ$  is readily converted to a powder. Its melting point is  $232^\circ$ , but it does not boil until  $2275^\circ$  (cf. other metals). Its specific gravity is 5.85. It can be prepared in three allotropic modifications (cf. iron). The malleable variety of tin is formed when tin is kept at temperatures above  $20^\circ \text{C.}$  and below  $170^\circ$ . If tin be cooled below that point it tends to pass into a gray crystalline variety with

an expansion in volume. This reaction is very slow indeed so that tin can be kept in the malleable form almost indefinitely, yet it is in a metastable condition. Strangely enough the speed of the change appears to increase with lowering of the temperature until it reaches a maximum at  $-48^{\circ}$ . It follows that block tin pipes will disintegrate and fall to powder at low temperatures. This change from metastable to stable form is facilitated by "inoculation," as is always the case with metastable forms, so that if once the change is initiated it proceeds fairly rapidly and gradually spreads. This change is known as "tin disease." The malleable tin is crystalline in the tetragonal system and if a stick of tin be bent a grating sound of the crystals rubbing upon one another is caused, known as "tin cry." At  $170^{\circ}$  or above, tin gradually changes into a rhombic variety known as "brittle tin," the formation of which is the cause of its brittleness at  $200^{\circ}$  previously mentioned.

Tin dissolves slowly in acids (see electromotive series), with oxidizing acids the result of treatment varies, *e.g.*, with dilute nitric acid, stannous nitrate is formed  $\text{Sn}(\text{NO}_3)_2$  but if not too concentrated acid be used tin is oxidized to stannic oxide,  $\text{SnO}_2$ , known as metastannic acid (*vide infra*). If very concentrated acid be used it is practically without action (see passive state of metals). Boiling alkalies slowly dissolve tin with liberation of hydrogen to form stannates (*q.v.*).

Tin has an atomic weight of 119, a weight arrived at not only by analysis of its oxides but also by its specific heat value, which is 0.055, and by its isomorphic relations with titanium. Tin is usually divalent in compounds in which it is a "positive" factor and is tetravalent in its acid forms. Its compounds are in certain cases distinctly amphoteric as is to be expected from its place in the periodic system.

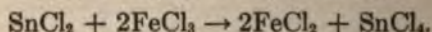
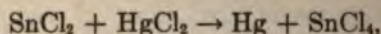
**Uses.**—Tin is made by the thousands of tons annually and used in a variety of ways; the most important being in the manufacture of "tin plate." This is made by dipping sheet iron, which has been carefully cleaned, into molten tin. A thin film of tin adheres to the surface of the iron and protects it, so long as the film is perfect, from the action of moist air. This tin plate is used for cans, drinking and cooking utensils, buckets, roofs, spouting, etc., etc. When a break occurs in the surface the iron rusts more rapidly than it would in the absence of the tin because of the electromotive forces set up. Copper and other metals



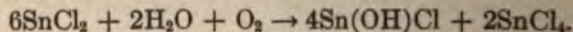
may be likewise tin plated. Tin is also used as material for making pipes, where freedom from corrosion or solution is demanded, as tin foil and for the manufacture of a long list of alloys.

**Compounds. Alloys.**— Tin amalgam is used in making mirrors. For this purpose tin foil is pressed upon glass plates and, after mercury is poured over it, is rolled until the amalgam adheres closely to the glass. The better grade mirrors are now silvered. The most important alloy of tin is solder, which is manufactured with varying proportions of tin and of lead for special purposes. (For other alloys see table of alloys, Appendix.)

**Halides of Tin.**— There are two series of tin halides of which only the chlorides are important. Stannous chloride,  $\text{SnCl}_2$ , is formed when tin dissolves in hydrochloric acid. It forms colorless crystals,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . When heated the crystals partially hydrolyze, also when the aqueous solution is largely diluted. In the first case stannous oxychloride is formed and in the latter the basic hydroxychloride,  $\text{SnOHCl}$ , insoluble, is formed. It rather readily passes over to the stannic salt,  $\text{SnCl}_4$ , and is therefore frequently used as a reducing agent, particularly in iron analysis and with mercuric salts. The reactions being:

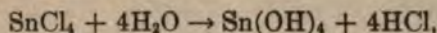


It is also oxidized by the air and in neutral solution the reaction may be expressed:



The stannic chloride hydrolyzes also, so that the precipitate formed is likely to be a mixture of stannic oxide and stannous oxychloride. All these reactions are reversed by the presence of an excess of hydrochloric acid and presence of metallic tin prevents oxidation to the stannic salt. If the stannous chloride, made by heating tin with hydrogen chloride gas, is heated it boils at a little above  $600^\circ$ . Stannous chloride will unite with iodine to form  $\text{SnCl}_2\text{I}_2$ . Stannic chloride is a fuming colorless liquid, b.p.  $113.9^\circ$ . It is made by heating tin with an excess of chlorine. It will unite with water to form a series of hydrates

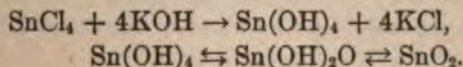
containing 3, 5 and 8 molecules of water. It hydrolyzes completely on standing with water:



and the latter is readily dehydrated. It also readily forms double salts with the alkali chlorides of which  $\text{K}_2\text{SnCl}_6$  may serve as a type. The stannic chloride is to be regarded as a distinctly non-metallic chloride from the fact that in solution in water it is at first a non-conductor, *i.e.*, is not ionized. Of course as hydrolysis proceeds the solution becomes a conductor owing to the formation of hydrochloric acid. Both the stannic and stannous chlorides and their derivatives are used as mordants in dyeing. A **mordant** is a substance which is insoluble, or becomes insoluble, in contact with material to be dyed and adheres firmly to the material. When soluble colored substances are added, the mordant forms with it an insoluble colored compound, or lake. The use of mordants in cloth manufacture is very extensive, particularly with cotton and linen goods.

**Oxides and Hydroxides of Tin.**—When stannous salts are treated with bases the insoluble hydroxide is formed which with strong bases goes into solution forming salts, the stannites. These are unstable and difficult to obtain by crystallization. Indeed on boiling strong solutions of stannites simultaneous oxidation and reduction takes place (*cf.* chlorites) and stannates and metallic tin are formed. By heating stannous hydroxide or stannous oxalate,  $\text{SnC}_2\text{O}_4$ , in the absence of air the black stannous oxide  $\text{SnO}$  is formed. Stannous hydroxide also dissolves readily in acids. It is thus amphoteric and is more markedly basic than acidic.

Stannic hydroxide is not known in pure form. When stannic chloride is treated with bases a jelly-like mass is precipitated which is probably the substance but it gradually loses water until the oxide  $\text{SnO}_2$  remains. This acts as an acid anhydride and dissolves readily in strong bases to form stannates of the formula  $\text{M}_2\text{SnO}_3$ . We have then this series of changes:



When treated with acids the stannic salts may be formed. The precipitate is known as stannic acid. When tin or tin alloys are



treated with nitric acid, there is precipitated an oxide of the same formula as above,  $\text{Sn} + 4\text{HNO}_3 \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} + 4\text{NO}_2$ , but which possesses somewhat different properties. It will not dissolve readily in either bases or acids. This is known as parastannic acid or more frequently as "metastannic acid." Historically this is interesting as being the earliest known case of isomerism, having been observed by Berzelius in 1811, and commented upon by him as demonstrating that identity of composition is not necessarily accompanied by identity of properties. It may easily be that these differences are due to difference in the size of the particles since specimens of intermediate character are readily obtainable. The present accepted explanation is that the difference is due to polymerization, *i.e.*, in the case of the  $\beta$ -acid several molecules of the oxide are combined to form a larger one; perhaps the  $\alpha$ -acid is  $\text{SnO}_2$  and the  $\beta$ -acid,  $(\text{SnO}_2)_n$ . This question may not be settled until we have some satisfactory method of determining molecular weights in the solid state. Freshly prepared oxide made at low temperatures is rather readily soluble in acid; if ignited it becomes wholly insoluble. This effect of ignition is also observed in the case of alumina and silica and to a less extent with iron oxide. The freshly formed oxide is white and while yellow if heated regains its whiteness on cooling. Tin oxide as found in nature is black and extremely inactive toward reagents.

**Fireproofing Fabrics.**— One of the most interesting uses of stannic oxide, as well because of its importance to human welfare as because of its chemical character, is in the fireproofing of cotton goods. Sodium metastannate solution, of specific gravity 1.225, is prepared and flannel or other inflammable material is soaked in the solution until thoroughly impregnated. After drying, this is soaked in a solution of ammonium sulfate and again dried. The ammonium stannate formed is hydrolyzed, giving a precipitate on the fibers of stannic oxide (*cf.* ammonium silicate, p. 268). No amount of washing with soap and hot water will remove it and the material cannot burn (see 8th International Congress Report, Vol. 28, p. 119). The cost of the process is said not to exceed a cent a yard. It would seem to be a cheap variety of fire insurance for small children.

**Other Compounds.**— Of the other compounds of tin mention may here be made only of the sulfides. Stannous sulfide, precipi-

tated from stannous salts by hydrogen sulfide is brown and is insoluble in sulfides of the alkalis. It is probable that the precipitate first thrown down is  $\text{Sn}(\text{SH})_2$  and this on drying loses hydrogen sulfide and becomes a black amorphous powder  $\text{SnS}$ . In the presence of polysulfides it adds sulfur to form stannic sulfide which dissolves to form metathioannates such as  $(\text{NH}_4)_2\text{SnS}_3$  from which stannic sulfide precipitates as a yellow amorphous powder upon acidification. Both sulfides so prepared are soluble in hydrochloric acid if of sufficient concentration and are hence not precipitated with hydrogen sulfide from tin salts if the solution be strongly acid.

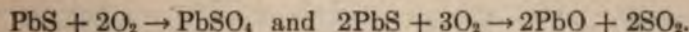
A very insoluble form of the sulfide may be obtained in crystalline form by heating tin amalgam with yellow sulfur and ammonium chloride. The mercury ammonium chloride and excess of sulfur volatilize on heating, leaving scales of a yellow substance known as "mosaic gold" or "bronze powder," much used for cheap decorations and as a pigment.

### LEAD

**Occurrence.**—Lead occurs chiefly in the form of **galena**,  $\text{PbS}$ . This is almost exclusively the commercial source of the metal. Smaller quantities occur as **cerussite**,  $\text{PbCO}_3$ ; as **crocoite**,  $\text{PbCrO}_4$ ; as **anglesite**,  $\text{PbSO}_4$  and **wulfenite**,  $\text{PbMoO}_4$ . There are also several other lead-bearing minerals. The ores are widespread and many different countries contribute to the world's supply of lead.

**History.**—Lead was one of the seven metals known to the ancients and like silver finds mention in the books of Moses. Lead was by the alchemists symbolized by the sign of the scythe,  $\text{♄}$ , the symbol of Saturn. It was used by the Romans to a small extent for the making of water pipes and kindred purposes.

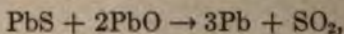
**Preparation.**—Lead is usually manufactured by first roasting the sulfide until it has been partially converted into lead sulfate and lead oxide. Two reactions are thus taking place simultaneously.



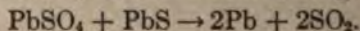
The mixture of lead sulfide, sulfate and oxide is then heated to a



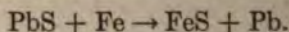
higher temperature without air supply. The reactions which take place result in the formation of metallic lead. These are:



and



Lead is sometimes produced by smelting the ore with scrap iron or with iron ores and coal. The essential reaction is



The iron sulfide melts and floats on the molten lead as a slag. Lead is also one of the products of the smelting of mixed ores as mentioned under silver (p. 431). As lead comes from the furnace it is usually alloyed with antimony, tin or other metals. The major portion of these impurities is usually removed by "softening," *i.e.*, by heating the lead in a shallow furnace in contact with the air until the impurities are oxidized and float on the surface as a scum which may be skimmed off. Or Parke's process (see silver) may be used. At Trail, in B.C., the refining of the pig lead is done by electrolysis. The bath used is hydrofluosilicic acid.

**Properties.** — Lead is a dull, gray, very soft metal. Its luster is fine when fresh but it speedily tarnishes due to the formation of a basic carbonate film on the surface. The tensile strength of the metal is so low that it cannot be used extensively as foil or wire. It is so soft that it may be scratched by the finger nail or disintegrated by friction against paper leaving a gray streak. The specific gravity varies, according to the method of working the metal, between 11.25 and 11.4. It melts at 326° C. and boils at 1525° C. When liquefied its specific gravity increases slightly, that is, the volume decreases. When subjected to pressure, therefore, it tends to liquefy and hence shavings may be pressed into compact masses and the metal is readily rolled or pressed into desired shapes. With a pressure of 33 tons per square inch it appears to liquefy at ordinary temperatures. If quickly cooled lead forms the amorphous body ordinarily encountered, but if cooled slowly or prepared by electrolysis it forms lustrous octahedral crystals.

Lead lies close to hydrogen in the electromotive series. It is then but slowly affected by acids as such and this action is further decreased, when hydrochloric or sulfuric acids are used, by the formation of the insoluble salts on the surface. It is

readily oxidized and then converted to the nitrate by nitric acid. In concentrated, hot sulfuric acid it dissolves readily with the formation of acid lead sulfate  $\text{Pb}(\text{HSO}_4)_2$  and in hot solutions of hydrochloric acid, since lead chloride is soluble in hot water.

All lead salts are poisonous and for this reason lead is not a very desirable material for utensils for food or beverages. It may be used for holding or carrying liquids since, if the liquids contain traces of carbonates or carbon dioxide, an adherent film of basic carbonate protects the lead surface from continued action. Free carbonic acid in considerable amounts may produce the formation of acid carbonate which is sufficiently soluble to cause trouble. Very pure water also dissolves lead sufficiently to render it dangerous for continuous use. As a poison, lead and its salts are distinctly and markedly cumulative and hence their continued contact with the body in any form is fraught with danger.

Lead oxidizes superficially in the air. It is supposed that the sub-oxide  $\text{Pb}_2\text{O}$  is first formed (*cf.* p. 556), which by contact with the moisture of the air is converted into a basic carbonate. This is doubtful. The equivalent weight of lead, determined by analysis of its chloride is, according to the best determinations, about 103.55 and by Dulong and Petit's law, since the specific heat is 0.0309, the atomic weight is twice this amount, 207.1. The vapor density of lead as determined at about  $2000^\circ$  indicates that its molecules are monatomic. Very recently the investigations at the Gibbs laboratory by Professor Richards indicate that lead from radio-active sources (*vide* Chapter XXXVI) has a lower atomic weight, indeed as low as 206.4. (See Journal American Chemical Society, Vol. 36, p. 1329). This fact has an important connection with the theory of evolution of the elements.

**Compounds. Halides.**—As a bivalent metal lead forms a series of halides  $\text{PbX}_2$  which are readily produced by treatment of the hydroxide or carbonate with the corresponding acids or by precipitation of soluble lead salts with soluble halides. These halides are comparatively insoluble in water at room temperature and increase in solubility with increase of temperature. The approximate values in grams per liter are:

	$\text{PbF}_2$	$\text{PbCl}_2$	$\text{PbBr}_2$	$\text{PbI}_2$
18°	5.22	10.0	7.5	0.7
100°	....	33.4	47.5	4.4

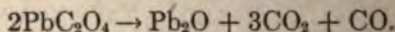


The salts precipitated by the cooling of the hot solutions are beautifully crystalline. These salts are but little hydrolyzed by water and show marked indications of partial ionization,  $\text{PbCl}_2 \rightleftharpoons \text{PbCl}^+ + \text{Cl}^- \rightleftharpoons \text{Pb}^{++} + \text{Cl}^-$ . They also readily form double halides with the alkali halides and acids and hence are more soluble in water containing these substances in spite of the tendency of a common ion to reverse the above equilibrium system.

As a tetravalent element lead also forms the halide series  $\text{Pb}_4$ . These halides are less stable than the bivalent salts and are readily and completely hydrolyzed by water. They are not, therefore, readily prepared in the pure form. The tetrachloride may be prepared by treatment of lead peroxide,  $\text{PbO}_2$ , with cold hydrochloric acid. The solution probably contains  $\text{H}_2\text{PbCl}_6$ . This solution by addition of ammonium chloride precipitates a salt  $(\text{NH}_4)_2\text{PbCl}_6$  which when dissolved in cold concentrated sulfuric acid liberates hydrochloric acid and a yellow oil which sinks beneath the acid (sp. gr. 3.18). This chloride fumes in moist air and reacts with water to produce lead peroxide,  $\text{PbCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{HCl}$ . If but little water is present plumbous chloride and chlorine are formed. These halides all readily form double halides, *e.g.*,  $(\text{NH}_4)_2\text{PbF}_6$ , etc. (*cf.* silicon, tin, boron and platinum halides).

**Oxides and Hydroxides.**— There are five compounds of lead and oxygen to which have been assigned the following formulae,  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Pb}_2\text{O}_3$  and  $\text{PbO}_2$ .

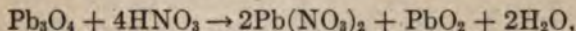
When lead oxalate is heated gently the reaction which occurs is perhaps,



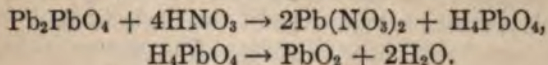
The product is dark gray and is not affected by water. For various reasons (and in particular because when treated with acetic acid, lead acetate and lead are produced and the heat of reaction is 10,000 cal., while the formation of lead acetate from lead oxide,  $\text{PbO}$ , is 15,500 cal., which involves a **negative** heat of formation of  $\text{Pb}_2\text{O}$  of 5500 cal.) it is considered most probable that the substance is a mixture of  $\text{PbO}$  and  $\text{Pb}$  (*cf.* similar suboxides of silver, bismuth, etc.).

Lead monoxide,  $\text{PbO}$ , is known also as **litharge** and as **massicot**. This oxide is one of the natural compounds of lead and is formed when any higher oxide is heated to  $600^\circ$  or upwards. It is also formed by the cupellation of lead. In this case the partially sub-

litharge. The yellow powder formed when the carbonate or nitrate is heated is the form sold as **massicot**. The oxide is strongly basic and absorbs carbon dioxide from the air. It also shows faintly acid character by dissolving in alkali hydroxide to form salts known as plumbites,  $2\text{NaOH} + \text{PbO} \rightleftharpoons \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O}$ , soluble in water, but reprecipitating the oxide on cooling. It does not react with water to form the hydroxide but the latter is readily precipitated from solutions of lead salts by bases. It is slightly soluble in water and is basic in reaction. On heating the oxide is formed. The litharge finds extensive commercial use in the preparation of boiled linseed oil, in the manufacture of cut and other varieties of glass, for paint preparation and the manufacture of lead salts. Red lead, or minium,  $\text{Pb}_3\text{O}_4$ , is not, properly speaking, an oxide but a salt. It is formed by roasting lead in the air at just below red heat. The reaction,  $6\text{PbO} + \text{O}_2 \rightleftharpoons 2\text{Pb}_3\text{O}_4$ , is reversible and the dissociation pressures are at  $445^\circ$ , 5 mm., at  $500^\circ$ , 60 mm., at  $555^\circ$ , 183 mm. Therefore at or below  $525^\circ$  the red lead is formed while above  $550^\circ$  it decomposes to form the litharge. If the compound is treated with dilute nitric acid the reaction,



takes place. It is evident from this that only one-third of the lead is acidic and therefore the compound is regarded as a salt of the acid  $\text{H}_4\text{PbO}_4$ , i.e., as  $\text{Pb}_2\text{PbO}_4$  or lead orthoplumbate and the above reaction probably takes place in two steps:



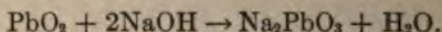
There is, therefore, no hydroxide of corresponding character. Red lead is very extensively used as a pigment, with linseed oil making a paint especially adapted to iron structures. It is also used as a "lute" in plumbing and as an oxidizing agent, especially in glass manufacture. Lead peroxide,  $\text{PbO}_2$ , is prepared as just described or, more cheaply by oxidizing a mixture of litharge and lime, thus forming calcium plumbate,  $4\text{CaO} + 2\text{PbO} + \text{O}_2 \rightarrow 2\text{Ca}_2\text{PbO}_4$ , which treated with dilute acid separates the peroxide.

The dioxide is an excellent oxidizing agent and in this connection finds varied application. When treated with dilute acid it gives no hydrogen peroxide and is hence regarded as having the structure



$\text{Pb} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ . It would seem there should be a true peroxide of lead  $\text{Pb} \begin{smallmatrix} \text{O} \\ | \\ \text{O} \end{smallmatrix}$

but it has not yet been prepared. The peroxide of lead corresponds to the tetrahydroxide  $\text{Pb}(\text{OH})_4$  or orthoplumbic acid. The free acid is not prepared but both ortho- and metaplumbates are known. The latter are readily formed by solution of the anhydride  $\text{PbO}_2$  in alkalies, *e.g.*,

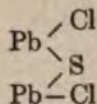


These salts are analogous to the metasilicates, metastannates and the carbonates. The chief interest attached to lead peroxide is the part it plays in the storage battery already discussed (p. 512).

**Lead Carbonates.**—The neutral carbonate,  $\text{PbCO}_3$ , is extremely insoluble and may be produced by precipitation from lead acetate solutions by the introduction of carbon dioxide. It is also formed by treatment of solutions of lead salts with sodium bicarbonate. If, however, the neutral carbonate of sodium is employed, the basic carbonate  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  is produced. This substance has been prepared and used as a pigment for many years under the name "white lead" and by reason of the opacity, covering power and durability of the paint prepared by mixing it with linseed oil is considered superior to any other white paint and indeed is often used as the "body" of many colored paints. It is prepared by various modifications of a method which will be sufficiently clear from a description of the "Dutch process." Sheet lead gratings are placed in earthenware pots above a shallow layer of vinegar, or dilute acetic acid. These pots are packed in layers with alternate layers of spent tan bark, or even manure, and allowed to stand for some months. The decay of the tan bark produces carbon dioxide and some elevation of temperature. The rise of temperature vaporizes acetic acid which converts a superficial layer of the lead to the acetate. The acetate is by the carbon dioxide converted into a porous mass of the basic salt and the acetic acid is freed to again attack the lead. In the course of time the lead gratings are wholly converted to the carbonate, after which the pots are removed and the carbonate finely ground and sold. The mixing with oil is carried out either by the painter on the "job" or, more commonly, is used in ready mixed form. It is these grinding and mixing processes which bring the workmen into contact with the white lead and produce the painful and occasionally fatal disease known as lead poisoning.

**Lead Acetate**, or sugar of lead,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , is an important salt. It has a sweetish taste and is used variously in medicine. It is soluble in water and hence a convenient soluble lead salt for the preparation of other and insoluble salts. It is a frequently employed component of hair dyes but its use is not without danger.

**Lead Sulfide**,  $\text{PbS}$ , is produced by the action of soluble sulfides upon lead salts and is frequently employed as a means of detection of lead. It is formed when white lead paints are subject to the action of air which contains traces of hydrogen sulfide. This fact accounts for the few white houses in cities. A sulfide of lead is sometimes precipitated from soluble lead salts which has the composition indicated:



This substance is reddish brown in color. The sulfide of lead is soluble in dilute nitric acid but is insoluble in hydrochloric acid. Nevertheless hydrogen sulfide precipitates lead sulfide with difficulty from solutions containing only a small excess of free acid, a fact of importance in qualitative analysis. Galena, the natural sulfide is, as has been mentioned, a most important mineral.

**Other Salts.**—**Lead Sulfate**,  $\text{PbSO}_4$ , is encountered as an adulterant of white lead, as a factor in qualitative analysis, and more particularly in the storage battery. It is soluble in concentrated sulfuric acid, forming the acid salt  $\text{Pb}(\text{HSO}_4)_2$  and in ammonium acetate solutions.

**Lead Nitrate**,  $\text{Pb}(\text{NO}_3)_2$ , is frequently employed as a laboratory reagent and as a starting point for the preparation of lead salts particularly of the chromate  $\text{PbCrO}_4$ . This latter salt is used extensively as pigment under the name of "chrome yellow." It is prepared at present by the **Luckow process** which consists in electrolyzing lead anodes in a solution of potassium chromate and common salt.

**Lead Arsenates**, of which there are three, the ortho- meta- and pyrosalts are used extensively as insectides in horticulture.



## SUB-GROUP B

**Titanium: Occurrence and History.** — Titanium does not occur free in nature, nor in large masses, but in small quantities it is extremely widely distributed especially in granitic rocks and their decomposition products. The iron minerals, magnetite,  $\text{Fe}_3\text{O}_4$ , and hematite,  $\text{Fe}_2\text{O}_3$ , frequently contain enough to interfere seriously with their utilization as ores of iron.

The most important mineral forms are rutile,  $\text{TiO}_2$ , ilmenite,  $\text{FeTiO}_3$ , and titanite,  $\text{CaTiSiO}_6$ . The dioxide also occurs in the polymorphic forms brookite and anatase. The recognition of the existence of a new "earth" in magnetic iron sand was due to McGregor, 1791, but rutile was first analyzed by Klaproth, 1794, and the metal termed titanium, from the giants of old. The metal itself was first isolated by Berzelius, 1825.

**Preparation, Properties and Uses.** — The element may be prepared by reduction of the oxide with carbon though a very high temperature is required, for which the electric furnace is most suitable. It is also prepared by the Goldschmidt process. The metal oxidizes readily at high temperature and also combines with nitrogen. An alloy of titanium and iron known as ferrotitanium is prepared, by the smelting of titaniferous iron ores, which contains 10 to 15 per cent of titanium. This is used as is ferromanganese to "purify" bessemer steel (see Bessemer process). The small quantity of titanium, 0.05 per cent, remaining in the steel improves its quality. If the percentage is at all considerable, up to 0.2 per cent, the product is known as titanium steel and is used in special constructions.

**Compounds of Titanium.** — Titanium is essentially tetravalent and its compounds, e.g.,  $\text{TiCl}_4$ ,  $\text{Ti}(\text{SO}_4)_3$ , etc., are analogous to those of silicon and tin. The hydroxide  $\text{Ti}(\text{OH})_4$  is precipitated by bases from titanic salts and does not dissolve in the excess of base. It is, therefore, a weak acid. The titanic compounds are reduced by nascent hydrogen to trivalent form, e.g.,  $\text{TiCl}_3$ , with the development of a violet color. A series of bivalent salts is also known. The soluble salts of titanium when treated with hydrogen peroxide are converted into a yellow soluble compound and the intensity of this coloration is made the basis for a quantitative estimation of the titanium present. The yellow color is sometimes presumed to be due to the formation of the trioxide  $\text{TiO}_3$ , but it is more reasonable to expect it to be a peracid analogous to Caro's acid and persulfuric acid.

**Zirconium.** — Like titanium, zirconium was also recognized and named by Klaproth, 1788, and was isolated by Berzelius, 1826. The name is derived from the most important mineral zircon,  $\text{ZrSiO}_4$ . The zirconium salts are analogous to those of titanium. The metal is also isolated in the same manner. The oxide, zirconia,  $\text{ZrO}_2$ , can be used as a factor in gas mantle construction (see cerium) in the Nernst lamp filament and in the preparation of refractory crucibles. The ores being rare and the preparation expensive the uses of the metal or of its com-

pounds are very limited. The **Nernst lamp** at one time promised to become a very important factor in lighting. Its special feature is a small rod made of the oxides of rare earths, chiefly zirconia, which glows brilliantly when heated to incandescence. The rod is at ordinary temperature a nonconductor and must be first heated. The heating is accomplished by means of a platinum wire which forms a core in the zirconia rod. The lamp is more efficient than the carbon lamp but it is less efficient than the tantalum and tungsten lamps and will probably never come into general use. Its chief interest is that the rod apparently acts as a conductor of the second class but the products of the electrolysis are wholly recombined as fast as formed. It appears, therefore, to function as a conductor of the first class.

**Cerium.** — The occurrence and other details concerning cerium have been presented on p. 527, and in this connection it remains only to call attention to certain special points. Its oxide was discovered by Klaproth in 1803 shortly after the discovery of the planet Ceres (1801) and hence was called ceria. Its salts are of two series in one of which the element is trivalent and in the other tetravalent. Both oxides are basic, the trivalent form most markedly as is usual. The nitrate is converted, by heating, to the oxide and the latter finds use in the Welsbach mantle (see thorium). The metal itself is usually prepared by electrolysis of the chloride, but may also be prepared by the Goldschmidt method. Its alloy with iron is used for gas and cigar lighters since it produces by friction, sparks similar to those produced by the ancient flint and steel. The temperature of the spark is higher, however, and readily ignites gas or alcohol vapor.

**Thorium.** — Thorium was discovered by Berzelius in a mineral, afterward called thorite, and was named in honor of the Scandinavian god Thor. Its properties are very similar to those of zirconium. It is found in a number of rare minerals and is of considerable special interest. Its oxide mixed with from 1 per cent to 2 per cent ceria constitutes the framework of the **Welsbach mantle**. To prepare the mantle the mixed nitrates are dissolved in water and cotton cloth (or more frequently ramie fiber) is saturated with the solution and allowed to dry. The mantles are formed and then burned. The cellulose is burned and the nitrates are converted to the oxides. These mantles are very brittle, and, for transportation, are dipped in collodion and dried. The collodion is burned when the mantle is first used. The mixture of cerium oxide and thorium oxide possesses specially high luminosity when heated to incandescence and the luminosity increases as the fifth power of the temperature.

Thorium is also of interest because of its relation to radium and uranium and like these possesses radioactivity (see Chapter XXXIII.)

**The Welsbach Mantle** has a particular interest since the separate oxides possess no special illuminating power. For example, a mantle made wholly of cerium oxide gives only seven candlepower light and of thorium only four candlepower when the mixture of 99 per cent  $\text{ThO}_2$  and 1 per cent  $\text{CeO}_2$  gives 80 to 100



candlepower for the same consumption of gas (120 to 130 liters per hour) and the light production falls off very materially with increase or decrease of the ceria content. Other materials than ceria produce like effects (*e.g.*, chromium, platinum, manganese, uranium, etc.), but are not suitable for use because the mantles are not so durable. Other materials than thoria may also be employed but are not practical for the same reason. An explanation of the high luminosity of Weisbach mantles is as follows: The mantle of pure thoria produces wave lengths at the temperature of the Bunsen gas flame which fall almost wholly in the infra-red portion of the spectrum. The pure ceria mantles while they produce some visible wave lengths also emit chiefly the nonvisible infra-red waves. The mixture of 99 per cent thoria and 1 per cent ceria emits only an extraordinarily small proportion of infra-red rays. This has the effect of diminishing the loss of heat by radiation so that the mantle is maintained at the temperature of the burning gas (1500 to 1600° C.), and hence more short or visible rays are produced. This influence upon the character of radiation is then a physical phenomenon and does not depend upon the chemical character of the mixture. (For fuller discussion see Abegg, Vol. III, pt. 2, p. 846 *et seq.*, and Le Chatelier, *Zeit. für Phys. Chem.*, Vol. 28, p. 566.)

**Exercises.** — 1. Explain how Dulong and Petit's law aids in the determination of the atomic weights of tin and of lead. Use the law in ascertaining the atomic weight of lead from the data, 103 g. of lead give 164.775 g. of dry lead nitrate. The specific heat of lead is 0.031.

2. Formulate the reactions which take place when lead peroxide is acted upon by sulfuric acid. Why is hydrogen peroxide not produced?

3. Explain any results which follow from the treatment of tin with dilute, moderately concentrated and very concentrated nitric acid; with lead acetate; with silver nitrate; with ferric chloride. Give equations where possible.

4. Pure stannic acid may be expected to have the formula  $\text{Sn}(\text{OH})_4$ . Explain the existence of a salt having the composition  $\text{Na}_2\text{Sn}_3\text{O}_{11}$ .

5. Explain in detail the reasons for the existence, for long periods, of malleable tin at temperatures below 20°.

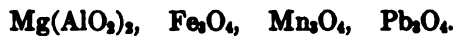
6. Write all the reactions involved in fireproofing cotton with sodium metastannate.

7. In the Luckow process for making lead chromate can you explain why the lead chromate by precipitation on the anode does not stop the process?

8. If lead has, according to source, three different atomic weights, what is the effect on the composition of lead chloride? Cal-

culate the percentage composition of radio-lead chloride and that of the chloride of ordinary lead.

9. Compare the structural formulæ of the compounds



10. Write equations representing the steps in the formation of white lead by the Dutch process.



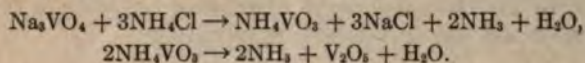
## CHAPTER XXXII

### SUB-GROUP A OF GROUPS V AND VI

In groups V and VI we have already presented the discussion of the type members and sub-group *B* and have now to take up in group V the three rare elements vanadium, niobium (columbium), and tantalum. They form a strongly marked sub-group having in general properties relating them to nitrogen. As is usual with the periodic groups metallic character increases with increasing atomic weight and decreasing valence. In sub-group *A* of group VI we have chromium, molybdenum, tungsten, and uranium. All these elements are of comparatively infrequent occurrence and the last three are usually classed as rare elements. They, or their alloys or compounds, have been found of many and varied uses and hence are familiar substances and their discussion must be in some detail. They present in general a marked contrast in many respects to the elements of sub-group *B*, the sulfur sub-group, and these differences are especially marked in the elements themselves and in compounds of lower valence. The last member, uranium, is particularly interesting because of its being the element of greatest atomic weight and because of its relation to the other members of series 12, the radioactive elements.

**Vanadium.** — The chief ore of vanadium is **vanadinite**,  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , which is the analogue of apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}(\text{F})$ . The element is, however, found rather widely distributed in granitic rocks and clays, but only in minute quantities. Vanadium was first observed by Del Rio in 1801 in a Mexican ore, but its discovery is usually ascribed to Seftstrom, 1830, by whom it was named after the Scandinavian goddess *Vanadis*. The chief present source is the ash of certain Peruvian coal, which contains as high as 48 per cent  $\text{V}_2\text{O}_5$ . It is a metal-like element with a silvery luster. Its specific gravity is 6.0 and melting point about  $1620^\circ$ . It is most readily prepared by the Goldschmidt method, using mixed metal (p. 533). Like nitrogen, it forms a series of oxides,  $\text{V}_2\text{O}$ ,  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_5$ . As with nitrogen and phosphorus also the higher oxides are acid in character and the pentoxide furnishes ortho-, meta-, and pyrosalts analogous to those of phosphoric acid (*q.v.*). The pentoxide is most readily obtained in the form of a cherry-red or yellow powder by treating sodium vanadate in solution with am-

monium chloride, ammonium metavanadate being precipitated. The ammonium salt is then heated. The reactions are:



The pentoxide is the usual starting point for the preparation of other compounds. There are frequently highly colored and very interesting types of compounds formed. Thus, as a bivalent element it forms a sulfate,  $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$ , isomorphous with the vitriols. The trivalent element forms a series of alums analogous with those of iron, chromium, and aluminium. Many and very complex derivatives are known. Vanadium compounds are used to some extent in the manufacture of certain dyes and also as catalytic agents. The chief use of the element is as a constituent of vanadium steel since a small percentage of it increases the malleability, hardness, and tensile strength of iron. To prepare the steel ferrovanadium containing from 7 to 13 per cent vanadium is made by reduction of the mixed oxides of iron and vanadium and is used as are ferrosilicon, ferromanganese, ferrotitanium, etc. (*Vide Steel*.)

**Niobium and Tantalum.** — There is found at Haddam, Connecticut, a mineral, known as columbite, which is an iron compound of the formula  $\text{Fe}(\text{CbTa})\text{O}_3$ . This mineral was first investigated and named by Hatchett, an Englishman, who determined in it the presence of a new element which he proposed to call columbium (from Columbia, *i.e.*, America). In 1802, Eckberg discovered in a mineral from Finland, to which he gave the name tantalite, a new element to which he gave the name tantalum, by reason of the difficulty with which its oxides react with solvents. (See the myth of Tantalus.) In 1844, Heinrich Rose investigated tantalite and succeeded in isolating from it two elements. He retained for one of these the name tantalum, as suggested by Eckberg, and gave to the other the name niobium (from Niobe, the daughter of Tantalus). He was either ignorant of, or ignored, the work of Hatchett. In consequence we find that both columbium and niobium are used as names for the same element. Both elements can be prepared by the Goldschmidt process or by a process devised by von Bolton. The latter method consists in heating a mixture of the oxides with paraffin and carbon, in vacuo, by means of the electric current. Two processes occur. The carbon reduces the higher oxide to a lower one and this last, being a conductor, is decomposed electrolytically, the metal and oxygen being produced. Niobium has a density of 12.75, a melting point of  $1950^\circ$ , and is somewhat malleable and ductile. It oxidizes slowly when heated in the air. Tantalum is similar to platinum in appearance, has a density of 16.6, and a melting point estimated at  $2900^\circ$ . It is more ductile than niobium.

The compounds of the two elements are such as are to be expected from their relation to vanadium and to sub-group B. Both elements are so rare that it is scarcely to be expected that they will be of extensive practical importance.

Tantalum in the form of very fine wire promised at one time to become of great value as a substitute for the carbon filament in incandescent lights. It is



an excellent conductor and the very long and fine filament necessarily used is very fragile. The efficiency of the lamp was very much greater than that of the carbon lamp. It was not long after its introduction before it was displaced by the still more efficient and more durable tungsten lamp.

### CHROMIUM

**Occurrence.** — The element does not occur free nor in a great variety or abundance of compounds. By far the most abundant form is **chromite**,  $\text{Fe}(\text{CrO}_2)_2$ , a compound isomorphous with spinel and magnetite. Other ores are **crocoite**,  $\text{PbCrO}_4$ , and **chrome ocre**,  $\text{Cr}_2\text{O}_3$ . Traces of chromium appear in serpentine, jade, and emerald, and the latter can be made artificially by use of molten alumina and chromium oxide. The same statement is also true concerning the ruby. In the two jewels the chromium appears to be in a different degree of oxidation. Almost all the chromium ore comes from Greece, New Caledonia, and Rhodesia.

**History.** — The element was first recognized by Vauquelin in crocoite in 1798 and in chromite by Fassett in 1799. It owes its name to the fact that all its compounds are colored (*χρῶμα* = colored).

**Preparation.** — Chromium oxide can be reduced in the electric furnace by carbon but is more conveniently prepared by the Goldschmidt process. The heat of the reaction is so great that the chromium is obtained in the molten condition. Most of the extensively used compounds are prepared, without the antecedent preparation of the metal, by fusion of chromite with oxidizing fluxes, and the resulting soluble chromate is used as a starting point for the preparation of the other compounds.

**Properties.** — Chromium is steel gray, very hard and very brittle. Its specific gravity is 6.50. Its melting point is about  $1490^\circ$ . It is fairly stable in air but heated to a high temperature oxidizes to the trioxide,  $\text{Cr}_2\text{O}_3$ . It dissolves in acids and appears to have a position in the electromotive series between aluminium and manganese (or between zinc and cadmium. See Alexander Smith's *Inorganic Chemistry*, p. 855). As an anode it dissolves during the process of electrolysis, according to Faraday's law, as a trivalent element, provided the density of the current is not too great, but if the current is moderately increased chromates are

produced. The metal also fails to dissolve in strong nitric acid. This is an example of metal passivity (see p. 601). Chromium forms at least three series of compounds in which it functions as a bivalent, trivalent, and hexavalent element respectively. Its compounds will be discussed under these three heads.

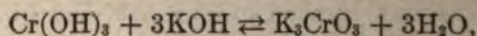
**Uses.** — Ferrochrome alloys are made by smelting chromite in the electric furnace, and this material, which may be made containing upwards of 60 per cent chromium, is used in the preparation of chrome steel. Steel containing from 2.5 to 4 per cent chromium is very hard and tough and is used in the manufacture of safes, ore crushers, stamps, car couplings, cutlery, and elsewhere where hardness and durability are essential. In pure form the chromium at present finds no special use, but its alloys play an important part in the construction of ordnance and armor plate. The ore, chromite, finds use in the construction of furnaces as a neutral refractory material. Other compounds find extensive use as mentioned below.

**Compounds.** — **Chromous compounds** are most readily prepared by dissolving chromium in hydrochloric acid, the hydrogen as it is evolved preventing oxidation to the chromic chloride.  $\text{Cr} + 2\text{HCl} \rightarrow \text{CrCl}_2 + \text{H}_2$ . The prevention of oxidation can be made more complete if some zinc is being dissolved at the same time. Chromic salts in acid solution may also be reduced by zinc to the chromous form. The addition of sodium acetate to chromous solutions precipitates the insoluble chromous acetate in the form of red crystals. Yellow chromous hydroxide may be precipitated from chromous salts by addition of bases. It oxidizes so readily that it slowly decomposes water, forming the chromic hydroxide and hydrogen,  $2\text{Cr}(\text{OH})_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Cr}(\text{OH})_3 + \text{H}_2$ . The chromous compounds are utilized chiefly as reducing agents.

**Chromic compounds**, derived from the oxide  $\text{Cr}_2\text{O}_3$ , are the most stable form of chromium salts. They are analogous in a general way to the corresponding salts of aluminium and of iron and in the analytical processes these three elements are of very similar behavior, a fact not accounted for by their periodic relations. Chromic salts of all the ordinary acids are presumably possible and most of these salts exhibit a remarkable peculiarity. They may be prepared in two modifications which differ from



each other in many properties. They have, however, the same formulæ. We have already encountered this in the case of the two varieties of stannic acid. Thus, if chromic oxide and carbon are heated together in a current of chlorine beautiful violet scales of the chloride are obtained as a sublimate,  $\text{Cr}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \rightarrow 2\text{CrCl}_3 + 3\text{CO}$ . This form is insoluble in water, though on long standing it will dissolve, and more rapidly if a trace of chromous salt is present. The solution is green. From this solution green crystals,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , may be separated, though ordinarily the crystals deposited are grayish-blue in color and the solution of these is violet in color. The green crystals in solution when treated with silver nitrate lose but one-third of their chlorine content. The gray-blue crystals in solution precipitate all the chlorine present as silver chloride when treated with silver nitrate. Many other salts of chromium likewise exist in these two modifications. This relation will be discussed more fully (see Werner's hypothesis). The hydroxide of chromium,  $\text{Cr}(\text{OH})_3$ , is precipitated from solutions of chromium salts by the addition of soluble bases. With excess of the stronger bases there is some solution with the formation of chromites (*cf.* aluminium),



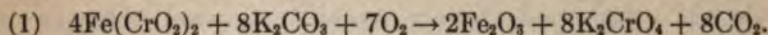
but the acidic character of the chromic hydroxide is so slight that on boiling the hydroxide is reprecipitated through hydrolysis. When chromic hydroxide is heated with basic oxides metachromites can be prepared and one of these, chromite, is the commonest natural compound of chromium. The relations may be expressed:  $\text{Cr}(\text{OH})_3 \rightarrow \text{CrO} \cdot \text{OH} + \text{H}_2\text{O}$ , and  $2\text{CrOOH} + \text{FeO} \rightarrow \text{Fe}(\text{CrO}_2)_2 + \text{H}_2\text{O}$ .

Chromic oxide,  $\text{Cr}_2\text{O}_3$ , may be prepared by dehydration of the hydroxide, by heating ammonium dichromate,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$  (*cf.* p. 268), or by reduction of potassium dichromate with sulfur. It is a most excellent green pigment, but since it is quite expensive most of the so-called "chrome green" paints found on the market are a mixture of chrome yellow, lead chromate,  $\text{PbCrO}_4$ , and Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

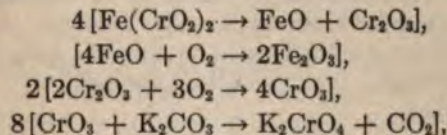
Of the other compounds mention need only be made of chromium acetate,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$ , used in the textile industry as a mordant, chromium sulfate,  $\text{Cr}_2(\text{SO}_4)_3$ , which exists in two modifications and several degrees of hydration of crystals, and chrome alum,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . The chrome alum is isomorphous

with the other alums and is especially valuable because on hydrolysis it yields the hydroxide and this in turn acts on skins in much the same manner as tannic acid from tan-bark. The alum is therefore much used to produce what is known as "chrome tanned" leather. Sodium bichromate, with reducing agents, is also used for the same purpose. It is to be recalled that like aluminium and ferric salts the carbonates, sulfides, and other salts of weak acids are not formed by precipitation methods and even the acetate is hydrolyzed completely on boiling.

**Acids of Chromium.** — The starting point for the preparation of practically all chromium compounds is through the preparation of potassium chromate by the fusion of potassium carbonate and chromite in the presence of air. Lime or limestone is usually added in order that the porous character of the lime may facilitate the access of air. The reaction which takes place may be indicated:



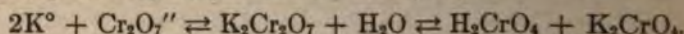
This rather complex equation may be simplified by considering it fractionally:



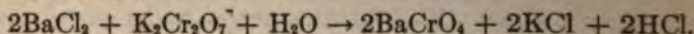
and by addition we get the equation (1) above. In case lime is also used any calcium chromate is converted to potassium chromate by treating the fused mass, while still hot, with a solution of potassium sulfate. The chromate is then dissolved in water and recovered by crystallization. It is a pale yellow salt which is very soluble in water, and isomorphous with potassium sulfate. When chromates are treated with acids they are converted to dichromates and since the latter are less soluble than the neutral salt and are not isomorphous with the sulfate, the dichromate is ordinarily prepared. When potassium chromate is treated with sulfuric acid the first change which might be expected is  $\text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{KHCrO}_4$ . This acid salt is apparently unstable and has not been prepared but, instead, we get by elimination of water from two molecules of the acid salt the dichromate,  $2\text{KHCrO}_4 \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$ . This salt, the most im-



portant chromium compound, is prepared on a very large scale. It crystallizes, without water of crystallization, in orange-red plates. Its solubility in water is 80 grams per liter at 10°, rapidly increasing with rise of temperature (50 g. at 0° and 129 g. at 100°). The corresponding sodium salt is very much more soluble and crystallizes with two molecules of water. The dichromate in solution in water ionizes to produce the relatively stable ion  $\text{Cr}_2\text{O}_7^{2-}$ , though by analogy with the behavior of the pyrosulfates and pyrophosphates hydrolysis should occur, thus:

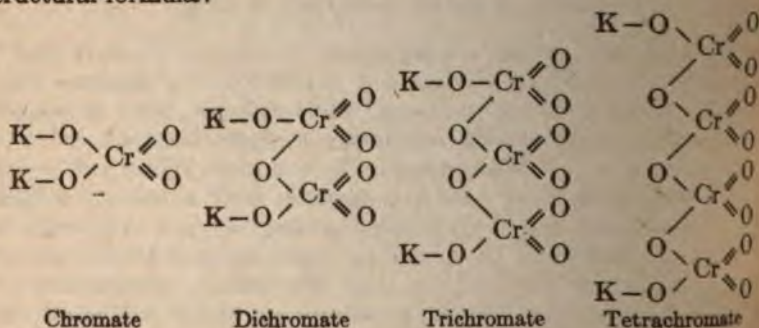


That such hydrolysis does occur is indicated by the fact that when salts of metals which form insoluble chromates are added to bichromate solutions, the chromate and not the bichromate is produced, *e.g.*,

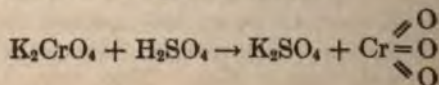


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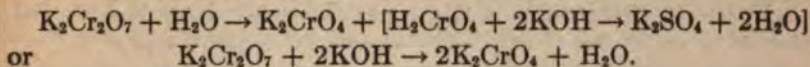
On the other hand, various methods of investigation indicate that in the absence of influences which withdraw chromate ions the hydrolysis, even in great dilution, does not go far. The bichromate is also convertible, by addition of chromic anhydride, or by appropriate treatment with acids, into the polychromates, and with concentrated sulfuric acid to chromic anhydride. These relations are probably most clearly expressed by the following structural formulæ:



The anhydride formation may be indicated:

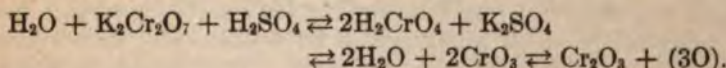


Bichromates are converted at once by addition of bases into the chromates. This may be taken also as an indication of at least minimal hydrolysis, *e.g.*,

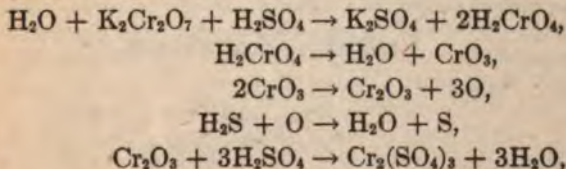


Alkali bichromates are, in general, stable toward heat since they melt without appreciable decomposition, the potassium salt at 400°. At higher temperatures, however, they decompose, forming first the products indicated:  $4\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 4\text{K}_2\text{CrO}_4 + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$ , and if the temperature be sufficiently high,  $4\text{K}_2\text{CrO}_4 \rightarrow 2\text{K}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$ .

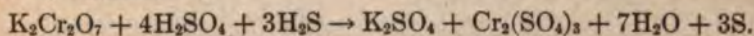
In solution in the presence of acids we have, of course, the tendency to form chromic acid. This is a powerful oxidizing agent probably by reason of its instability, with consequent formation of the anhydride, and of the instability of the latter. Oxidizing reactions of acidified chromate and bichromate solutions are therefore to be considered as the disturbance of the following equilibrium system by oxidizable substances:



Oxygen is not present in such a system to an extent involving its evolution in the free condition. If, however, oxidizable substances are present withdrawal of oxygen involves the movement of the system in the direction  $\rightarrow$ . The equations representing such reactions appear at first rather complicated but if factored are rather simple, *e.g.*,



and by summation,



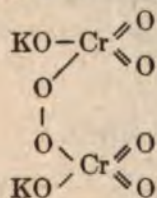
By use of this system of relations the oxidation reactions of the bichromates may be readily expressed in the form of equations. This somewhat detailed consideration has been given the chromates



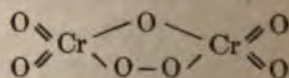
because of their extreme importance as laboratory reagents, particularly in quantitative analysis and in organic preparations.

**Chromic Anhydride,  $\text{CrO}_3$ ,** separates in the form of dark red needles, if an excess of concentrated sulfuric acid be added to concentrated solutions of bichromates or chromates. It is a powerful oxidizing agent and ignites alcohol, decomposes ammonia, chars paper and in general strongly resembles sulfur trioxide. One of its modes of behavior is utilized to distinguish chlorine from iodine and bromine. If a dichromate and chloride are mixed and treated with concentrated sulfuric acid and distilled, a dark red liquid, boiling at  $116^\circ$ , distills over. It is chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , the analogue of sulphuryl chloride. It may be collected in water by which it is hydrolyzed,  $\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{H}_2\text{CrO}_4$ . The corresponding iodine and bromine compounds have not been made. The chromyl fluoride is known.

**Perchromic Acid.**—The deep blue solution obtained when dilute solutions of chromic acid are treated with hydrogen peroxide, which was discovered by Barriswill in 1847 and is used as a means of detection of small quantities of both chromates and hydrogen peroxide, is a very unstable substance. It is soluble in ether, in which it is less evanescent. The blue solution was shown by Moissan to be perchromic anhydride,  $\text{Cr}_2\text{O}_7$ , but is not necessarily a heptavalent derivative of chromium. If it is treated with acetates of metals, at sufficiently low temperature, compounds are produced having the empirical composition  $\text{M}'\text{CrO}_4$ , where  $\text{M}'$  is a univalent metal. These salts are extremely unstable and have probably the structure represented by, *e.g.*,



and the anhydride may be



that is to say, the compounds contain the hydrogen peroxide grouping  $-\text{O}-\text{O}-$  and the probable molecular formula  $\text{M}'_2\text{Cr}_2\text{O}_8$ . By use of concentrated hydrogen peroxide fairly stable salts of the formula  $\text{K}_3\text{CrO}_8$  have also been prepared.

## MOLYBDENUM

**Occurrence.** — Molybdenite,  $\text{MoS}_2$ , and wulfenite,  $\text{PbMoO}_4$ , are the most important ores of molybdenum. The former was long confused with graphite, plumbago, or "black lead." The name, from this fact (from  $\mu\omicron\lambda\upsilon\beta\delta\alpha\iota\tau\alpha$  = lead), we owe to Scheele who first recognized the existence of a special acid-forming element in molybdenite. The discovery of the element is usually ascribed to Hjelm, who first isolated the element in 1790.

**Preparation, Properties and Uses.** — The element can be obtained from its oxide by reduction with charcoal, but is most readily prepared by the Goldschmidt process. Its specific gravity is approximately 8.6 and its melting point about  $2500^\circ$ . As a pure metal it finds almost no practical uses, but its alloys, especially that with iron, are useful. Molybdenum steel, containing up to 10 per cent molybdenum, is used to make rifle barrels, propeller shafts for ships and other vehicles and more especially, tool steels. It is said to be more suitable for the latter purpose, because less brittle, than tungsten steel (*q.v.*). The world war has greatly stimulated its production.

**Compounds.** — When molybdenite is roasted the oxide,  $\text{MoO}_3$ , is produced. It is the most important of molybdenum compounds. Like chromium trioxide, it is a distinctly acidic oxide and with bases forms molybdates. Ammonium molybdate in nitric acid solution is used very extensively as a means of estimation of phosphates. The precipitate formed when this solution is added to phosphates is a voluminous yellow phosphomolybdate. This substance varies in composition somewhat according to the conditions of precipitation, but is approximately  $(\text{NH}_4)_3\text{PO}_4 \cdot 11\text{MoO}_3 \cdot 6\text{H}_2\text{O}$ . The variation from constancy is ascribed usually to the facility with which the acids of this group form "condensed" or "poly" acids. It may, however, be considered that we have here an example of the law of definite proportions functioning simply as a "definition," since not only the phosphomolybdate, but the analogous compounds of arsenious, arsenic, silicic, vanadic, tantallic, tungstic acids form similarly variable compounds, although beautifully crystalline and otherwise characteristically "definite compounds." Other degrees of oxidation of molybdenum are represented by the chlorides  $\text{MoCl}_2$ ,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$  and the oxides corresponding to these. By means of zinc and acid, *i.e.*, "nascent hydrogen," all the higher forms are reduced to the trivalent stage with color changes ranging through violet to blue or black. Likewise in acid solution the sulfide,  $\text{MoS}_2$ , is produced by hydrogen sulfide, though its precipitation is preceded by the formation of a blue color, thought to be due to molybdenum molybdate,  $\text{Mo}(\text{MoO}_4)_2$ . The sulfide is somewhat soluble and consequently the element may appear also in group IV, since it is soluble also in ammonium sulfide. Since molybdates when acidified produce molybdic acid, which in turn forms the fairly insoluble trioxide, molybdates may appear in the first analytical group. This behavior makes molybdenum a very unwelcome factor in quantitative operations.



The compounds of molybdenum find use as pigments in china painting, as a mordant in dyeing, in coloring leather and rubber, and especially in analytical laboratories as a reagent.

### TUNGSTEN

**Occurrence and History.** — The two chief ores of tungsten, scheelite,  $\text{CaWO}_4$ , and wolframite,  $(\text{FeMn})\text{WO}_4$ , are fairly abundant minerals and the recent development of extensive uses of the element and its compounds has induced a considerable production. (In 1915 upwards of 5000 tons of the metal.) Its production being much greater than that of mercury, bismuth and cadmium combined, it is evidently out of place to longer consider it a rare element. The element was discovered in 1781 by Scheele in the mineral then known as "tungsten," hence the name. The German name for the element is wolfram, hence the symbol W. It is said to have been a constituent of "Damascus" steel.

**Preparation, Properties and Uses.** — Tungsten ores can be converted into soluble tungstates by fusion with sodium carbonate. The soluble salt can in turn be precipitated by treatment with acids, as tungstic acid,  $\text{H}_2\text{WO}_4$ , and this in turn by heating may be converted into the oxide,  $\text{WO}_3$ . The metal may be prepared in the form of a powder by reduction of its oxide by means of either hydrogen or carbon. It may also be, and usually is, prepared by the Goldschmidt process. The metal is very heavy (sp. gr. 18 to 19.6) and very infusible, melting point about  $3000^\circ$ , and is ordinarily very hard but by proper mechanical treatment may be tempered to a softness about equal to that of platinum. The powdered metal may be converted into a compact form by first forming an amalgam which is molded into the desired form and then the mercury is expelled by heating, leaving the tungsten in coherent form. The powder may also be pressed into compact form and then welded by hammering or rolling while at a high temperature. The softened metal is ductile and may be drawn out into wire. It is a fairly good conductor of electricity. It is not acted upon by the air readily at high temperatures, nor does it volatilize to an appreciable extent even at very high temperature. If, therefore, long thin wires are properly supported and are heated by the electric current, a very high temperature, and consequently high luminosity, may be obtained. This is particularly true if the

lamp bulb is filled with nitrogen; better still, with argon. The relative efficiency of these lights is shown by the comparison: the best carbon lamp consumes 2.5 watts per candlepower, tantalum lamps, 2.0 watts, and the tungsten about 1.2 watts. This saving in cost of lighting has made the tungsten lamp almost universally used and many millions, even hundreds of millions, are annually produced. There is now reported an arc light type of an incandescent lamp which uses tungsten and certain oxides of the rare earths for which an efficiency of 0.3 watt per candlepower is claimed. (See Sci. Amer. Supp., Vol. 81, p. 109 (1916).) Tungsten iron alloys are of special importance for the manufacture of tungsten steel, which is an alloy of tungsten (16 to 20 per cent), chromium (2.5 to 5 per cent), vanadium (0.35 to 1.5 per cent), carbon (0.55 to 0.75 per cent) and iron (72.75 to 80.6 per cent), possesses the property of being tempered to extreme hardness and does not lose its "temper" when hot. It may therefore be used for turning tools for high-speed lathes. Its introduction has vastly cheapened the production of many types of machines (automobiles, for example), and has fairly revolutionized shop practice (cf. molybdenum steel).

**Compounds.** — While tungsten as an element is characteristically metallic, its compounds, particularly those in which its higher valencies are expressed are acid in character. In a general way they resemble those of molybdenum and at least four chlorides, and the corresponding oxides, are described. The tendency to form complex compounds of indefinite character is even more marked than with molybdic acid. Besides the normal tungstate of sodium,  $\text{Na}_2\text{WO}_4$ , at least thirteen others have been described, all of which contain smaller proportions of tungsten. Sodium tungstate is used as a mordant in dyeing and for fireproofing fabrics (cf. p. 552). By partial reduction of sodium or potassium tungstates in acid solution by means of tin, the so-called "tungsten bronzes" are obtained. These range in color, according to mode of preparation, from yellow to blue, violet and purple. These bronzes are not true tungstates, nor are they tungstites. One of them, for example, is said to have the composition  $\text{Na}_2\text{W}_4\text{O}_{12}$ . Phosphotungstic acid,  $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot 18\text{H}_2\text{O}$ , is a crystalline soluble substance which is used as a reagent for alkaloids and proteins. Tungsten compounds are used to some extent as pigments. The trioxide is "canary yellow" in color.



## URANIUM

**Occurrence and History.** — The most important ore of uranium is pitchblende, or uraninite, a complex mineral (see p. 464), which contains the uranium as the oxide,  $U_3O_8$ . Other ores, now of special importance because of radium (see Chap. XXXIII), are cleveite, a mineral of the pitchblende type, which contains also yttrium and other rare earths, also interesting because of the presence in it of helium, carnotite, a potassium uranate and vanadate, and samarskite, a uranium Tantalum-niobate. The element was first observed by Klaproth in 1789 and named after the then newly discovered planet Uranus. It was first isolated by Peligot in 1842.

**Preparation, Properties, and Uses.** — The element may be prepared by reduction of the tetrachloride by sodium, or from the oxide by carbon in the electric furnace. It is a white metal resembling nickel, not as hard as steel, of a specific gravity about 18.7, melting point about  $1500^\circ$ . As a metal it has no special applications as yet but its alloy with iron has special hardness and toughness, which would doubtless find uses were uranium more common. The special interest attached to uranium is its association with radium, into which it apparently is continually decomposing. This relation and accompanying features is the special topic of the next chapter. It is also of interest as being the element possessing the maximum known atomic weight.

**Compounds.** — Uranium forms a long series of compounds derived from the stages of oxidation represented by  $U_3O_8$ ,  $UO_3$ ,  $U_2O_5$ ,  $UO_4$  and  $UO_2$ . It will be observed that in the last of these it shows the maximum valency as if it belonged to group VIII. The more readily formed salts are those derived from  $UO_2$  and  $UO_3$ , the uranyl and uranic salts. The more common uranium salts are of uranyl,  $UO_2$ . Examples are uranyl nitrate,  $UO_2(NO_3)_2 \cdot 3H_2O$  and uranyl acetate,  $UO_2(C_2H_3O_2)_2$ . (Cf. bismuthyl and antimonyl salts.) These are sometimes used in the quantitative estimation of phosphoric acid. The most important compound of uranium is sodium diuranate,  $Na_2U_2O_7 \cdot 7H_2O$  (analogous to the dichromates), which is used in making uranium glass, which shows a very beautiful greenish-yellow fluorescence.

**Exercises.** — 1. Discuss the conditions which affect the color of compounds in solution.

2. Why are chromium sulfate and nitrate stable in water solution while the sulfide is not?

3. If sodium hydroxide is added to solutions of the following compounds, what happens and why? Chromic nitrate, chromic acid, potassium chromate, potassium dichromate?

4. Assuming the cost of current at ten cents per kilowatt per hour, how much would be the saving per night of twelve hours by



using the tungsten lamp as compared with the best carbon lamp if ten thousand candle power light is used?

5. Formulate the reactions involved in the preparation of the metals of this group by the Goldschmidt process.

6. Since the phosphomolybdate precipitate is of inconstant composition unless under very carefully controlled conditions, what are the probable reasons for its utilization in the estimation of phosphates?

7. Consider and state the advantages from an economic standpoint of tungsten and molybdenum steel as turning tools.



## CHAPTER XXXIII

### RADIOACTIVITY

As has already been mentioned the members of the eleventh series of the Mendeleeff system possess radioactive properties and a discussion of these and certain connected phenomena and deductions therefrom is the purpose of the present chapter. Though the topic is relatively very new its intensely interesting and important character has produced an enormous amount of investigation and an even more enormous amount of conjecture. A brief historical résumé will place us in a position to intelligently consider the more definite phases of the topic.

**Cathode Rays and the Electron Hypothesis.** — During the period from approximately 1850 to 1897, the investigation of the discharge of electricity between electrodes sealed in highly evacuated tubes (Fig. 124) developed facts concerning

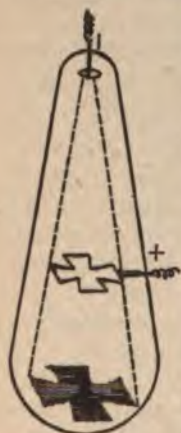


FIG. 124.

what are known as the cathode rays as follows: The cathode gives rise to particles which, when they strike the glass surface of the tube, render it phosphorescent; a shadow is cast upon the walls of the tube when certain kinds of substances, *e.g.*, platinum, are placed between the cathode and the opposite wall of the tube; the particles, when they are concentrated upon an object, raise its temperature; they produce chemical changes in many substances; they can pass through thin sheets of metal but the absorptive power is proportional to the density of the metal employed; they charge negatively an electroscope placed in their path, and their course is deflected by the positive pole of an electromagnet. They will cause a fog when the cathode stream is directed into moist air; above all,

these particles seem to be the same whatever the nature of the cathode employed. A portion of these extremely remarkable facts led Crooks (1879) to assume that they represented a **fourth state**

of matter, which he called radiant matter. Based upon the deflection of cathode rays by means of a magnet, J. J. Thompson estimated their velocity at approximately that of light and estimated their mass as  $\frac{1}{1836}$  that of the hydrogen atom. He reached the remarkable conclusion (1897) that **cathode rays are negatively charged electrons** (a term suggested by Stoney (1881)), which **have been formed by the disintegration of atoms**. From this beginning and from the study of the behavior of radioactive substances has been subsequently developed the conception of atomic structure later detailed (Chap. XXXVI). These studies have also led to the conception that electricity is itself corpuscular and these electrons are nothing else but particles of electricity. This idea has been incorporated with the ionization hypothesis and we are inclined to regard a positive ion as a portion of matter differing from the ordinary substance by one or more electrons, while particles are rendered anions by addition of negative electrons.

This addition of the electron hypothesis to the ionic has somewhat the character of "piling Ossa on Pelion," but if it can be successfully done and a better "aussichtsturm" so obtained there can be little objection. The danger lies in the tendency to assume that by so doing new knowledge is gained, a condition contrary to fact.

**X-Rays.** — When cathode rays impinge on glass or other surfaces a manifestation of energy known as X- or Roentgen rays (discovered by Roentgen 1895) is produced. These rays have remarkable penetrative power. They pass through glass and other solid matter and are not deflected by the magnet. They move with the velocity of light and are capable of producing photographic effects similar to those of light. They are not visible rays but falling on many substances they produce a fluorescence by which their presence may be detected. Such substances are barium platinocyanide  $\text{BaPt}(\text{CN})_4$ , calcium tungstate,  $\text{CaWO}_4$ , sphalerite,  $\text{ZnS}$ , etc. These X-rays appear to be radiant energy of very short wave lengths ( $10^{-8}$  cm.) and have recently been subjected to diffraction by "crystal gratings," by W. L. Bragg and his son, through which operation much tentative information has been gained about crystal structure.

The full discussion of X-rays and their properties is of course no function of a text on chemistry, but so much is needed for a presentation of radioactivity. The part played in chemistry by



X-ray study is doubtless only a beginning. (See atomic numbers, p. 625.)

**Canal Rays.**—In the vacuum tubes beside the cathode rays another set of rays arise at the anode and travel in straight lines with a velocity apparently  $\frac{1}{10}$  that of light. They appear to be positive "electrons," *i.e.*, are deflected by the negative pole of a magnet. Their mass is not constant for different anodes and they appear to consist of particles ranging from the mass of the hydrogen to that of the helium atom.

**Radioactive Substances.**—In 1896 Henri Becquerel attempted to discover if the substances made fluorescent by X-rays would themselves produce X-rays, *i.e.*, if the change were of the reversible type. He used for his purpose uranium salts and discovered that if these salts were placed on photographic plates for some hours and then the plates were developed the outlines of the salt masses were shown on the plate. These effects were shown to be produced by all uranium compounds and by the metal itself. It was inferred that the results were due to radiations from the substances, which were hence called radioactive, and that these radiations (called Becquerel rays) were similar to X-rays. They were, however, able to discharge a charged electroscope (Fig. 125) and this simple and long known instrument



FIG. 125.

has proved the most effective for ascertaining traces of radioactivity in minerals.

Using this method the radioactivity of thorium and of its compounds was discovered in 1898 (by Schmidt and Madame Curie independently) and also that certain uranium ores were more radioactive than pure uranium or its pure salts. Professor and Madame Curie then undertook the investigation of one of these to determine if the activity were due to an "impurity." Pitchblende was selected, since its activity was about seven times that of uranium. The very laborious and trying investigation resulted, as was indicated in Chapter XXVI, in the isolation of salts of a new metal several million times more active than uranium. The difficulties encountered are but faintly indicated by the fact that

from 6000 kg. (6 long tons) only 2 g. of pure radium bromide can be obtained.

**Nature of Radiation.** — Investigation of the radioactivity of radium compounds by the Curies, by Rutherford, Boltwood, McCoy (and of recent years by almost countless others) has developed such a very large number of facts (and so much speculation) that it is not possible to go into full detail. The following points may be regarded as clearly established:

The radiations from active materials are of three kinds, known as  $\alpha$ ,  $\beta$  and  $\gamma$  rays.

The  $\alpha$  rays are of the same general type as anode, or canal, rays, i.e., they are of an initial velocity about  $\frac{1}{10}$  that of light, carry positive electrical charges, double that on the hydrogen ion, and are of approximately 4 times its mass. They are quickly stopped by solid substances and even by air and when they are discharged they prove to be identical with helium. Indeed Ramsay and Soddy have shown that the rate of production is 158 cubic millimeters per gram of radium per year. The flashes of light produced in a spinthariscopes (Fig. 126) are supposed to be due to the impact of  $\alpha$  particles from a bit of radium salt upon zinc blende.



FIG. 126.

The  $\beta$  rays are identical with the cathode rays. In terms then of the electron hypothesis they consist of negative electricity moving with the speed of light (apparently they move more rapidly than cathode rays).

Both  $\alpha$  and  $\beta$  rays cause fog precipitation in moist but dustless air (cf. p. 274) when the air is suddenly cooled by expansion; and C. T. R. Wilson has been able to photograph these "fog tracks" which apparently indicate the paths of moving molecules.

The  $\gamma$  rays are identical with X-rays and are presumed to be produced, as are the latter, by impact of  $\beta$  rays, or electrons, on surrounding matter.

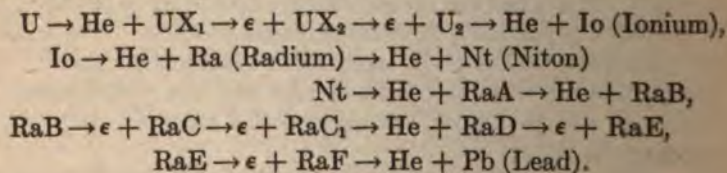
The most striking fact about radioactivity is that it is not apparently influenced in the slightest by anything which can be done to it. It is as rapid at  $-200^{\circ}$  C. as at  $2000^{\circ}$ , nor does light or electrical or chemical treatment alter its rate. Nevertheless, heat is being constantly evolved from radium at a rate approximately equal to 120 calories per hour per gram of radium.



Besides these "rays" Rutherford has shown that radium also produces an "emanation" or gas which can be liquefied and otherwise investigated. It proves to be without any detectable chemical properties. It was given the name niton and assigned to a vacant place in the zero group in the periodic system. It is itself radioactive and decomposes after a few days, giving a radioactive solid and helium.

Every uranium mineral contains radium and radium emanation and on treatment of nearly all these minerals with reagents which effect their solution helium gas is evolved. Also when uranium compounds are treated with reagents which effect the removal of the radium the uranium radiation can be reduced to a minimum and indeed to a point where practically only  $\alpha$  particles, i.e., electrically charged helium, are produced. After from six months to a year the radioactivity of the uranium salt regains its original activity.

**Theory of Radioactivity.** — The above facts have led to the following conclusions more or less well established by supplementary evidence from various sources: While uranium, radium, and other substances (*vide infra*) are regarded as elements since they have the general behavior of such in the chemical sense, they are yet regarded as decomposing into simpler elementary forms. The end products are electrons, helium and, finally, lead. The energy liberated is presumably due to *intra* atomic changes, while the ordinary forms of chemical change involve energy because of interatomic relations. More or less certainly it has been established that the series of changes from uranium to lead involve the following steps:



The symbol  $\epsilon$  above is intended to represent an electron  ${}_{-1}^0\text{e}$  the hydrogen atom in weight. The transformation from uranium to lead therefore represents a loss of 8 helium atoms ( $\text{He}^{00}$ ) and since lead, helium when free, and uranium are all neutral in the various stages above given a total of 16 electrons are given off.

A similar series of decomposition products from thorium have also been assumed; also ultimately ending in lead. In this case the assumption is that there are lost by the thorium 6 helium atoms and consequently 12 electrons.

Two other series of decomposition products are also possible, derived from the elements actinium and polonium. These elements occupy the vacant places in the periodic system in series eleven, but their existence is not yet sufficiently well established that they appear in the international tables of atomic weights (1917).

That such a decidedly revolutionary view of the character of radioactivity and of the decomposition of elements should have so quickly gained practically general scientific assent is due to a number of supplementary lines of evidence a few of which are as follows:

The electron hypothesis has received rather general acceptance as an instrument for the coördination of physical facts of both electrical and magnetic types. The coincidence of properties of the products of electrical discharge in highly evacuated tubes with those of many of those of radioactive decomposition inevitably connect the two types of phenomena and the two hypotheses support each other (*cf.* p. 581). Radium, and its less stable derivatives, appear to decompose at a rate which can be accurately measured and their half-periods, calculated on the basis of monomolecular reactions (*cf.* p. 137), give life periods which account for various well established facts. For example, no uranium ores are known which do not contain both radium and lead. Also no thorium ores are known which do not contain lead. If however lead from these two sources is converted into lead chloride and the atomic weight determined, that from thorium ores gives an atomic weight of 208.4 (Soddy) while that from radium ores gives values ranging from 206.4 to 207.15 (Richards and Lambert, *Jour. Am. Chem. Soc.*, 36, 1329). Ordinary lead has an atomic weight of 207.20. This evidence is the stronger because uranium by loss of 8 helium atoms (or a total loss of  $4 \times 8 = 32$ ) should give an atomic weight of  $238.2 - 32 = 206.2$ , while thorium by loss of 6 helium atoms (a total of 24) should give an atomic weight of  $232.4 - 24 = 208.4$ .

The character of the work and that of the investigators is such that we must accept the fact that there are at least three varieties of lead chloride with identical properties, so far as has been determined, and yet with varying proportions by weight.



This exception to the law of definite proportions must apparently be accepted as a fact. Moreover, we are also faced by an apparent situation where one of the fundamental points of Dalton's atomic hypothesis will not apply. The atoms of lead are not all of like weight. Elements having different atomic weights but the same chemical characters are called **Isotopes**. (This assumption of unlike atoms is also used by Crooks to account for the varying properties of the nearly related rare earths (*q.v.*) which Crooks proposes to call "meta elements.")

The heat evolved by radioactive decompositions is not to be accounted for satisfactorily except by the assumption of atomic disintegration, for were these radioactive substances really helides, as Armstrong supposes, *i.e.*, really compounds of lead or other elements with helium, it is not credible that such enormously endothermic compounds would decompose at rates uncontrolled by external conditions. It is estimated, for example, on the basis of the known heat evolution of radium and its calculated life, that one gram of radium on decomposition yields not far from 2,000,000,000 calories of heat, a quantity approximately a quarter of a million times that of the combustion of a like quantity of carbon.

Finally, it may be said that geologists and astronomers are unable to account for the relatively slow cooling of the sun and of the earth. It would appear from fossil remains that life has existed on the earth so many million years that it should be cooler than it is. But from considerations based upon the decomposition of elements not only is it rendered probable that this source of heat accounts for the discrepancy but we are transferred to the other horn of the dilemma and are confronted with calculations which would lead to the conclusion that the world should be growing warmer. For details of the properties of the radioactive elements as known up to 1911, see Soddy, "Chemistry of the Radio Active Elements," Longmans, Green & Co.

**Theory of Atomic Structure.** — Based on considerations derived from the electron hypothesis and radioactive phenomena, J. J. Thompson has reached the conclusion that atoms are concentric rings of negatively charged electrons revolving about a central positive charge of electricity. The atom may thus be compared to a planetary system. The stable atoms are in equilibrium while the large systems represented by the elements of

the eleventh series are in unstable equilibrium. This conception involves the acceptance of the electron as the primordial form of matter and involves the possibility of decomposition of the atoms of the more stable elements, provided only a sufficient concentration of energy can be brought to bear upon them. Ramsay considered that this can be done, and is done, by the action of radioactive substances upon other elements. It is to be regretted that experimental data sufficient adequately to support this hypothesis is not yet at hand but its lack is not surprising and for it we must await the accumulations of years of scientific research. Meanwhile, it is a stimulating and imagination-gripping possibility.

**The Life Term of Elements.**—In the series of products of the disintegration of uranium given on p. 582 the estimates based upon the "half period" of the products give the following life period.

U.....	8,000,000,000 years	RaA.....	4.3 minutes
Ux.....	35.5 days	RaB.....	38.5 minutes
U <sub>x2</sub> .....	1.65 minutes	RaC.....	28.1 minutes
U <sub>1</sub> .....	3,000,000 years	RaC <sub>1</sub> .....	10 <sup>-4</sup> seconds
Io.....	200,000 years	RaD.....	24 years
Nt.....	5.5 days	RaE.....	7.2 days
Ra.....	2240 years	RaF.....	196 days
		Pb.....	unknown

These figures are, of course, only approximate and will be changed as more accurate data appear. They do, however, furnish data for many interesting speculations and conclusions. For example, **fergusonite**, a uranium mineral, contains enclosed helium in the ratio of 26 cc. per gram of uranium. On the basis of the rate of decomposition of uranium it is calculated that the age of the mineral is about 416 million years.

**Exercises.**—1. Carefully select the statements in this chapter and classify them under the heads: (1) Fact; (2) Probable fact; (3) Hypothesis.

2. Outline just how you would proceed to isolate radioactive material from a mineral.

3. How would you undertake to determine the existence of  $\alpha$ ,  $\beta$ , and  $\gamma$  rays in a given radioactive material?



## CHAPTER XXXIV

### GROUP VII

THE sole known representative of sub-group A of Group VII is manganese, though by all the indications of the periodic system three remain to be discovered (*cf.* p. 207, also p. 629, Chapter XXXVI). Manganese occurs rather abundantly in a large variety of compounds. The chief of these are **pyrolusite**,  $\text{MnO}_2$ , **hausmannite**,  $\text{Mn}_3\text{O}_4$ , **braunite**,  $\text{Mn}_2\text{O}_3$ , **manganite**,  $\text{MnOOH}$ , or  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , **manganese blende**,  $\text{MnS}$ , and **manganese spar**,  $\text{MnCO}_3$ . It is also frequently a "displacing" element in silicious rocks, substituting for both the trivalent and bivalent elements. Its oxides are therefore decomposition products of these rocks and accumulations fairly rich in manganese are known as **wad**. Small quantities of manganese are found in the ashes of plants. Traces of it also produce the color of many colored minerals of the amethyst type. The most important natural compound is the pyrolusite.

**History.** — Manganese compounds have been long used. The Egyptians apparently used them for decolorizing, as well as coloring, glass. Its compounds were first distinguished from those of iron by Potts (1740). Scheele's investigations led Bergman to a realization of its elementary character, though it appears to have been first isolated by Gahn in 1774.

**Preparation, Properties, and Uses.** — The element may be prepared from its oxide by reduction with carbon or by means of magnesium or zinc. It is quite readily prepared, and most easily by the Goldschmidt process. Not much is prepared in the pure condition but enormous quantities are prepared by the smelting of mixed iron and manganese ores in the form of **spiegeleisen** (*q.v.*) and **ferromanganese**. The pure element is typically metallic in character; it is brittle, hard, and heavy (sp. gr. 7.2). Its melting point is  $1245^\circ$ . It is dissolved readily by acids with evolution of hydrogen. It decomposes steam at red heat.

Heated in the air it oxidizes readily. It also unites readily with nitrogen at high temperatures, forming a nitride. The element forms six series of compounds corresponding to all the possible valencies of the seventh group except the lowest (*cf.* p. 207). As the bivalent element it is a base-forming factor but with increasing valency acid properties appear and the heptoxide with water forms the extremely strong permanganic acid. It finds use only as an alloy.

**Alloys.** — Ferromanganese (70–80 per cent Mn) and spiegeleisen (5–15 per cent Mn) are used in the manufacture of bessemer steel (*q.v.*) and also for the manufacture of manganese steel. The latter contains varying percentages of manganese according to the purpose for which it is used. It finds special application in “burglar proof” safes, for ships’ shafting and propellers, and for rock-crushing machinery. Manganin (Cu 84 per cent, Mn 12 per cent, Ni 4 per cent) and similar alloys are used for resistance wires in electrical instruments. The Heusler alloys are a very remarkable set of alloys which are essentially copper, manganese, and aluminium, and are nearly as magnetic as iron itself.

**Manganous Compounds.** — The series of salts in which manganese is bivalent may be prepared either by dissolving the metal in acids or by reducing the compounds of higher valence in acid solution. The hydroxide,  $\text{Mn}(\text{OH})_2$ , is precipitated from manganous salts as a white amorphous substance, turning brown quickly by reason of oxidation. It is soluble in the presence of ammonium salts for the same reason that magnesium hydroxide is (*cf.* p. 471). The same statement also applies to the carbonate. The sulfide is insoluble in water but is soluble in dilute acids which fact places manganese in the third analytical group (p. 396).

The manganous salts are all pink in color under usual conditions. They are not very stable but oxidize less readily than the “ous” salts of chromium or iron. In the presence of powerful oxidizing agents they are converted to permanganic acid (*q.v.*). The sulfate,  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ , is a vitriol, while  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  is not.

**Manganic Compounds.** — The best representative of this class of manganese compounds is  $\text{Mn}(\text{OH})_3$  formed by oxidation by the air of ammoniacal solutions of manganous salts. The corresponding salts are unstable. An oxide,  $\text{Mn}_3\text{O}_4$ , hausmannite.

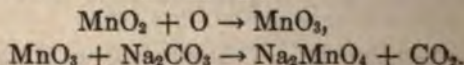


occurs in nature and is also formed by heating to redness the dioxide, or indeed when any oxide of manganese is strongly heated in the air. It is apparently a spinel and is a manganese manganite derived from  $\text{Mn}(\text{OH})_2$  by loss of one molecule of water,  $\text{Mn}(\text{OH})_2 - \text{H}_2\text{O} \rightarrow \text{MnOOH}$ , this by reaction with manganese hydroxide gives,  $2\text{HMnO}_2 + \text{Mn}(\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + \text{Mn}(\text{MnO}_2)_2$ , or,  $\text{Mn}_3\text{O}_4$  (cf. p. 523, spinel, p. 557, red lead, and p. 605, magnetite).

**Tetravalent manganese compounds** find their best representative in the dioxide,  $\text{MnO}_2$ . This is the natural compound pyrolusite. It is most readily prepared by gentle ignition of manganous nitrate. Its hydrated forms are prepared by oxidation of manganous salts by basic oxidizing agents, *e.g.*, sodium hypochlorite, or by reduction of permanganates in alkaline solution (cf. p. 590). The mineral is used as an oxidizing agent (cf. p. 116, chlorine), and in glass manufacture to compensate the green produced in glass by the presence of ferrous silicate. It is also used in black paints as a "dryer," *i.e.*, to oxidize, and hence harden, the oil. Its hydrated form,  $\text{Mn}(\text{OH})_4$ , might be expected to precipitate from alkaline solutions but this does not occur. Instead, hydrates possessing fewer hydroxyl groups are produced. Salts corresponding to these hydrates are formed, *e.g.*, with lime,  $\text{CaMn}_2\text{O}_5$  (cf. p. 116). These are known as manganites.

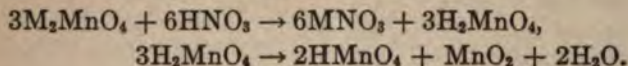
The structure of the dioxide is apparently  $\text{Mn} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$ , since with acids oxygen, and not hydrogen peroxide, is produced. It is conceivable that the isomeric form  $\text{Mn} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$  might exist. **Pentavalent**

**manganese compounds**, like univalent ones, are not certainly known. **Hexavalent compounds** find their best representatives in the salts of manganic acid,  $\text{H}_2\text{MnO}_4$ . The anhydride is not certainly known but is reported as a red unstable powder. The acid is also not known in the pure condition but when compounds of manganese are fused with sodium carbonate the following reactions are believed to take place, *e.g.*,



The manganates are intensely green compounds and the soluble salts give green solutions. These manganates are very unstable in solution and when placed in dilute solution or when an acid is

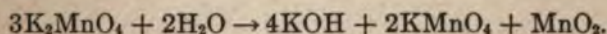
added a reaction takes place which is reminiscent of the behavior of hot hypochlorites and hypobromites though not exactly analogous. This reaction may be formulated:



If, then, we accept  $\begin{array}{c} \text{H}-\text{O} \\ \text{H}-\text{O} \end{array} \backslash \text{Mn} \begin{array}{c} \text{=O} \\ \text{=O} \end{array}$  as the probable structure of the evanescent manganic acid, analogous to sulfuric acid, and for the

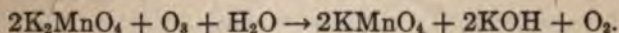
permanganic acid  $\text{H}-\text{O}-\text{Mn} \begin{array}{c} \text{=O} \\ \text{=O} \end{array}$ , we see that we have a case of

simultaneous auto oxidation and reduction with a change of valence of one atom of manganese from six to four and of two from six to seven. The change from the green manganates to pink permanganate may be followed by placing some of the powdered fused green mass in a tall cylinder full of water. The fused mass is sometimes called the chameleon mineral. The reaction may in this case be formulated:



If we consider manganic acid as an analogue of sulfuric acid we must observe that it is much weaker, as well as less stable, since water hydrolyzes its salts markedly.

**Heptavalent manganese** compounds find their best representative in potassium permanganate,  $\text{KMnO}_4$ . This compound is formed as above described and may also be prepared by passing ozone into the manganate solution, thus avoiding loss of manganese as the dioxide,



The permanganate may be obtained from the aqueous solution by crystallization. The acid corresponding to this salt,  $\text{HMnO}_4$ , is a very strong acid (p. 175), but is also unstable so that it is with difficulty prepared in the pure state. It may, however, be prepared by adding dilute sulfuric acid to a concentrated solution of barium permanganate and, after filtration, allowing the solution to evaporate spontaneously. It is obtained in the form of red crystals,  $\text{HMnO}_4 \cdot x\text{H}_2\text{O}$ . Dilute solutions of the acid are prepared by the action of powerful oxidizing agents upon manganese compounds,



e.g., with lead peroxide and sulfuric acid we have  $2\text{MnO}_2 + 3\text{PbO}_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{HMnO}_4 + 3\text{PbSO}_4 + 2\text{H}_2\text{O}$ . (Cf. Qualitative analysis.) Morse and Olsen (Am. Chem. Journal, Vol. 23, p. 431) obtained concentrated solutions by electrolyzing a solution of potassium permanganate in porous cups as indicated in Fig. 127. The special interest attaching to this process is that while the  $\text{MnO}_4^-$  ion travels into the anode cup and the  $\text{K}^+$  ion out of it, water also goes out (cf. p. 511), and the acid is simultaneously produced and concentrated. The permanganate in the solid form if treated with concentrated sulfuric acid gives an oily liquid, probably  $\text{Mn}_2\text{O}_7$ ;  $2\text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Mn}_2\text{O}_7$ . It is a very

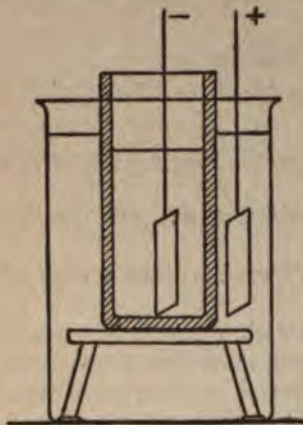
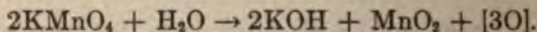


Fig. 127.

sensitive, highly explosive compound. It is also a very powerful oxidizing agent.

Potassium permanganate is itself an extremely powerful and very useful oxidizing agent, and may be used in either acid, neutral, or alkaline solutions. The degree of reduction is different in acid from that in neutral or alkaline solutions since in the former manganous salts,  $\text{Mn}^{++}$ , are produced and in the latter manganese dioxide is formed. The acid behavior may be formulated,  $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + [5\text{O}]$ , and this oxygen is then available for oxidation of whatever reducing material is present. The reaction proceeds very slowly if no withdrawal of the oxygen takes place, but more rapidly in the light than in the dark.

If in neutral or alkaline solution we have:



This type of reaction is encountered when the permanganate is exposed to the air or when it acts upon the skin or clothing. The curious case of the simultaneous reduction of each other by oxidizing agents may now be recalled with profit (cf. p. 92).

It will be observed that manganese is of somewhat protean chemical character and it may aid one to recognize this if we say that as a free element it is a metal of the type of iron, as a bivalent ion it behaves in a general way like magnesium, as a trivalent ion

it is similar to aluminium, chromium ( $\text{Cr}^{\text{+++}}$ ), and iron ( $\text{Fe}^{\text{+++}}$ ). As a tetravalent element it is similar to lead, as hexavalent, to sulfur in the same valence, and in the highest valence only does it show its character as a member of the seventh group.

**Exercises.** — 1. What is meant by the term "available oxygen" as applied to potassium permanganate and potassium dichromate, and how is it made available?

2. Outline the facts which lead to the assumption of the structure of permanganates.

3. Calculate the weight of potassium permanganate needed to make a normal solution when used (a) in acid solution, (b) in alkaline solution.

4. Write the equations for the reactions between potassium permanganate in sulfuric acid solution and (a) calcium oxalate, (b) sulfurous acid, (c) ferrous sulfate.

5. If required to prepare all the oxides of manganese explain in detail the steps for each.

6. Given a solution of potassium permanganate how would you undertake to obtain, (a) oxygen, (b) chlorine, (c) manganese dioxide, (d) manganese sulfate? Formulate the equations.



## CHAPTER XXXV

### GROUP VIII

THERE are three sub-groups in group VIII. Each forms one of Döbereiner's triads (p. 205). Each sub-group presents a set of three elements with closely related properties and with atomic weights which are much nearer the same values than successive elements usually show. All the members are true metals when non-valent and all show an approach toward a maximum valence of eight in their oxygen compounds, though stable octavalent compounds only are obtainable with ruthenium and osmium.

The first sub-group (Fe, Ni, Co) belongs to series 3 (p. 207) and are common elements. The second sub-group (Ru, Rh, Pd) are very rare elements and have relatively small technical value. The third (Os, Ir, Pt), while rare elements, are more extensively used in various ways. Since iron is so important that the present is sometimes referred to as the "iron age" its chemistry and its technology are vastly important and it will be considered in some detail. The other elements are treated more briefly.

#### IRON

**Occurrence.**—Iron is the fourth element in order of quantity found in the earth's lithosphere. It is found native, occasionally in large masses and more frequently in small quantities disseminated through basaltic rocks. Meteorites are frequently nearly pure iron alloyed with certain other metals, such as nickel, cobalt, and copper. The chief ores of iron are siderite,  $\text{FeCO}_3$ , hematite,  $\text{Fe}_2\text{O}_3$ , magnetite,  $\text{Fe}_3\text{O}_4$ , and limonite,  $\text{Fe}(\text{OH})_3$ . Siderite is not unfrequently mixed with bands of clay or coal and is then known as "ironstone" and "black band ore." Hematite is found in amorphous form as a soft earthy deposit, in hard massive form, and in black crystalline leaflets. The last is known as "specular iron" or as "micaceous hematite." Since the relation between limonite and hematite is that of the hydroxide and its dehydrated form it is not surprising that there are several intermediate min-

erals, such as **goethite**,  $\text{FeOOH}$ . Magnetite is frequently magnetized as found in nature and is the anciently known "lodestone." The quantity of these ores which is mined annually is stupendous. In the United States alone in 1917 75,500,000 tons were used. This gives only a faint notion of the place iron occupies in our industrial system. In spite of this enormous output of ores they are not the most common compounds of iron. The **iron pyrite**,  $\text{FeS}_2$ , is, at least in pure mineral form, the most abundant natural form of the element. It is not used as an ore. It occurs in two forms: the yellow variety, known as "fool's gold," and as **marcasite**. Iron is also widely distributed in the form of the more or less completely hydrated oxide in soils, which owe their colors to its presence. Iron is also a frequent constituent of both stratified and igneous rocks. The modes of formation of the great deposits of iron ore form one of the very interesting chapters of Geology (*vide* Le Conte's Geology). Iron is a constituent of many plant tissues and is also a constituent of animal tissue as well as of the blood of all "red blooded" animals.

**History.** — To write a complete history of iron were almost to write a history of the development of our race. It is not without reason that this is called the iron age and the importance of iron is not less even though we are emerged into what the future may call the "electrical age."

As far back as authentic history goes man was familiar with iron as a material for weapons of war and of the chase. At least 5000 years ago iron implements were used by the Egyptians. The myths of ancient times assign the knowledge of the use of iron as a gift of the gods. The mention of Tubal Cain (Genesis 4: 22) as an artificer in brass and iron indicates the remoteness of the discovery of iron even in the time of Moses. The alchemists also were accustomed to refer to Tubal Cain as the originator of their art. The alchemistic symbol for iron was, appropriately enough, the sign of the shield and spear of Mars,  $\text{♂}$ , which was also the astrological sign of the planet. The Latin name for iron, *ferrum*, gives us our symbol,  $\text{Fe}$ , and the terms *ferrous* and *ferric* as used for iron salts. The name iron appears to be of Scandinavian origin. Iron as originally used was probably meteoric, but the earliest source of manufactured iron appears to have been India. The Hindus apparently use the same smelting methods today which they used centuries since. Furnaces



for iron are mentioned by Moses (Deut. 4: 20) and appear to have been used in Spain centuries before the Roman conquest of the world. Modern smelting began in England about 1500 A.D., but the production was limited by the necessity of using charcoal as a fuel. The opening of the really modern era of progress dates from 1713 with the introduction of coke as a fuel. In 1828, Neilson introduced in Scotland the use of the hot blast which was a very

important forward step. In 1856 Bessemer invented the process which bears his name (*vide infra*) and which has had tremendous influence in modern development and on political history.

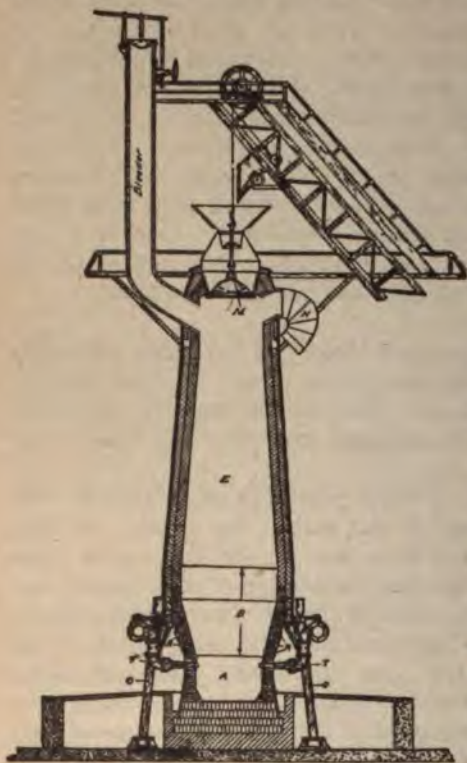


FIG. 128.

**Preparation.**—The story of the various methods used in the past for preparing iron and of those used at present by various peoples is too complicated to be presented here, but makes intensely interesting reading. (See *Manufacture of Iron and Steel in All Ages*: Swank.) The modern method with its tremendous output and vast machinery is alone too much for our present purpose. The attempt will be made only to outline the plan of operations.

Iron is smelted in a furnace the size of which may be as great as one hundred or more feet in height and 35 to 40 feet in diameter and capable of producing upwards of a thousand tons of iron daily. The construction of the furnace is indicated in the figure (Fig. 128).

Iron ore usually contains as gangue more or less silicious material and with it is charged into the furnace a sufficient quantity

of limestone to form a fusible mass, called a "slag," which not only permits the removal of the gangue in liquid form but assists the process of smelting. With the ore and limestone are added sufficient coke to effect the reduction of the ore and the fusion of the slag and iron. These are the raw materials entering at the top of the furnace. At the bottom is introduced air which has been preheated to  $1100^{\circ}$  by passage through "stoves" filled with checker work of tile and heated by the waste gas of the furnace. (See Fig. 129.)

In the furnace a rather complex series of changes take place, but essentially it may be represented by the equation:  $3C + Fe_2O_3 \rightarrow 2Fe + 3CO$ . The reduction of the iron takes place in the upper part of the furnace and is of course accompanied by the formation of some carbon dioxide. In the lower portion

of the furnace water\* from the atmosphere is decomposed by the hot iron and carbon, and some hydrogen is liberated. Also some cyanogen  $(CN)_2$  and hydrocarbons are formed so that the gas, as it issues from the top of the furnace, contains in addition to nitrogen (58 per cent) and carbon monoxide (about 25 per cent), also carbon dioxide (10 per cent), hydrogen (4.5 per cent), and other gases (2 per cent).

This gas is freed from dust and from most of the carbon dioxide, and is used as a fuel to run the furnace machinery and for many purposes about the plant, as well as to preheat the air. The iron as it passes down through the furnace is melted and in doing so absorbs a considerable amount of carbon and almost all of the phosphorus and sulfur present in the raw materials used. At the

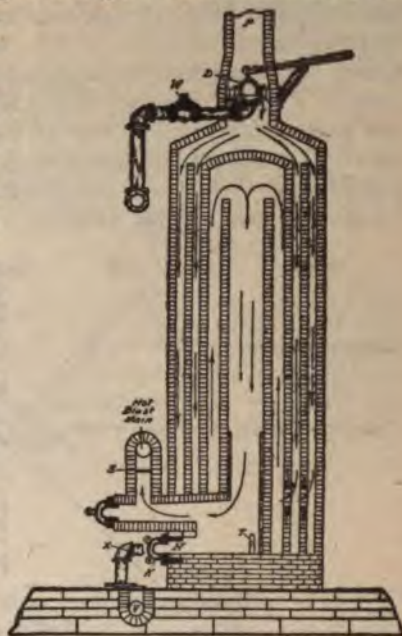


FIG. 129.

\* In most modern furnaces the Gayley dry air blast system (1904) is employed. It is said to effect a saving of about a dollar a ton in fuel since the decomposition of water absorbs heat (cf. water gas, p. 349).



same time with the iron some silicon is reduced, from the silica present, and alloys with the iron. The molten iron as drawn from the furnace is either at once conveyed to the proper place for utilization in the manufacture of iron and steel products or is cast into molds. The crude iron so produced is known as cast iron or "pig iron." The composition of the pig iron varies somewhat with the raw materials used, but the following is a typical analysis: Carbon 2.77 per cent, silicon 1.84 per cent, titanium 0.074 per cent, phosphorus 0.189 per cent, sulfur 0.035 per cent, manganese 0.744 per cent. The carbon is usually present chiefly in the

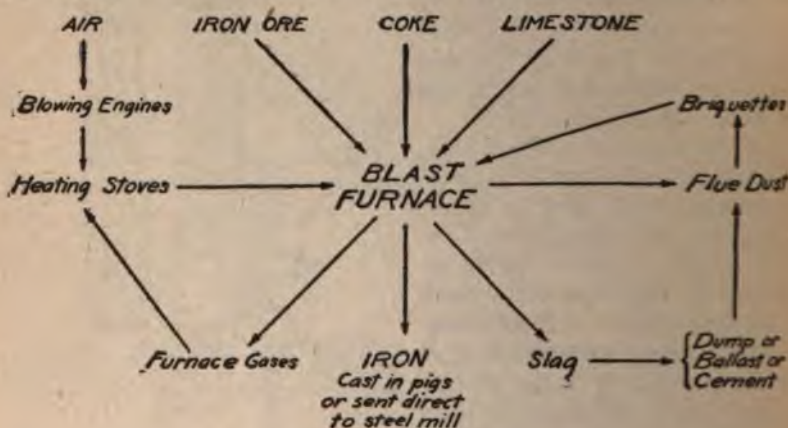


FIG. 130.

form of graphite. The slag produced by using the gangue of the ore with added flux is essentially a low-grade glass. It is about 55 per cent silica, 30 per cent lime and 15 per cent alumina. Its composition of course varies greatly. Slag is used for a variety of purposes, such as road metal, ballast, cement, etc. A diagram, taken from Benson's Industrial Chemistry, illustrates the relations of the raw materials and output of the furnace (Fig. 130).

**Refining of Iron.**—The product of the iron furnace, cast iron, finds many uses just as produced but the greater part is converted into a huge variety of products which may be roughly classed as malleable iron, soft steel, hard steel.

**Malleable iron or wrought iron** is, as the name indicates, capable of being readily worked. For this purpose it is necessary to remove

the silicon, carbon, phosphorus and sulfur so far as such removal is possible. The most extensively used method is known as pud-

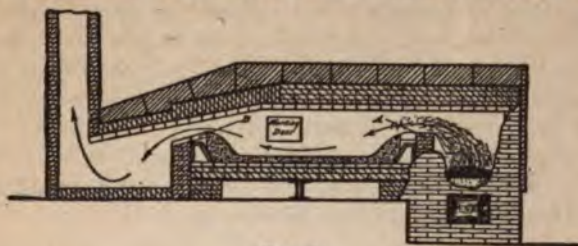


Fig. 131.

dling. The pig iron is placed in a reverberatory furnace (Fig. 131), along with "hammer scale,"  $\text{Fe}_3\text{O}_4$ , or other oxide of iron, and melted. It is stirred thoroughly in order to bring all portions in contact with the oxidizing flame playing on the surface. The temperature is maintained at such a point that when the impurities, so far as practicable, are burned out, the iron solidifies to a pasty mass which is then "balled up" and while hot rolled into the desired bar form. Such iron is not wholly pure but it must not contain more than 0.1 to 0.2 per cent carbon. If wrought iron contains more than a trace of phosphorus it is "cold short," *i.e.*, is brittle under the hammer when cold. If more than a trace of sulfur is present it is "hot short."

Soft steels are such as contain a low percentage of carbon and traces of other impurities. A typical analysis is, carbon 0.45 per cent, silicon 0.087 per cent, phosphorus 0.102 per cent, sulfur 0.066 per cent, manganese 0.916 per cent. There are two types of

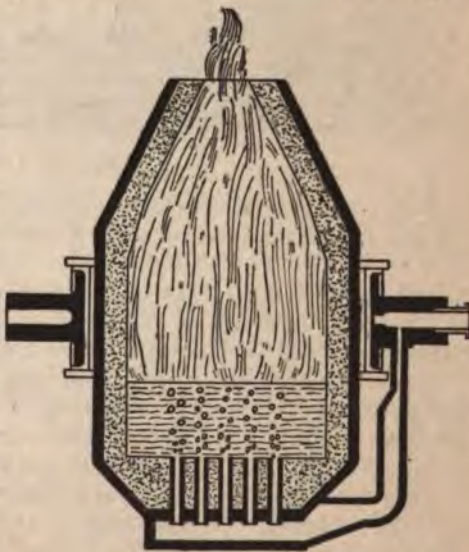


Fig. 132.



process in use known as the **Bessemer** and the **open hearth** processes. The principle employed in the Bessemer process, invented in 1856 by Henry Bessemer, is to place the iron in the molten condition in a converter, Fig. 132, and by means of a blast of air burn out the foreign particles and convert them into a fusible floating slag. The passage of air is stopped as soon as this is accomplished and, to remove traces of oxide so formed, "spiegel-eisen," an alloy of manganese and iron is added. (Chap. XXXIV.) The manganese present reduces the traces of iron oxide and any excess manganese remains in the steel.



FIG. 133.

The open hearth furnaces are called "acid" if lined with silicious material and "basic" if lined with bricks made essentially of burned dolomite (p. 450). In both these processes the melted metal is heated for a considerable length of time in a furnace of the type shown (Fig. 133). The oxidation of the impurities is by hot air heated by regenerative flues, *i.e.*, flues heated by the escaping gases. The final stage is the addition of manganese iron alloy as in the Bessemer method. The purpose of the basic lining is to absorb the phosphoric pentoxide formed by oxidation. In such case crude iron high in phosphorus may be used while in the acid process only low phosphorus iron may be used. This is not the proper place to discuss the various advantages of the different types of furnace, but it is sufficient to remark that both, as well as many modifications, find use.

**Hard steels** are of many kinds, but may be roughly divided into two groups, first, those in which hardness is due to combined

carbon and, second, those in which other metals confer desired properties on the product. Three methods of operation are in use, the cementation process, the crucible process, and the open hearth method.

In the oldest, or cementation process, the principle employed is to heat the wrought iron, not to the melting point, with carbon, usually charcoal. The iron gradually absorbs the carbon and when the desired amount is absorbed the process is stopped. The temperature maintained is about  $1000^{\circ}$  and the time required is from 8 to 11 days. The steel as it comes from the furnace is known as blister steel and after sorting is heated and rolled or hammered into bars of suitable size. It may be melted and cast into ingots. In the crucible steel method, wrought iron and carbon are heated in crucibles of graphite and clay. The molten iron absorbs the carbon and the whole operation takes about four hours. This method is also used for making special steels by adding small quantities of other metals such as nickel, manganese, etc. Electric furnaces are rapidly coming into use for the manufacture of special steels and in general for crucible steel. High carbon steel is also made by the open hearth processes.

Pure iron, it will be observed, is not made by any of the processes so far described. Indeed, pure iron is not known commercially and only by the greatest care can it be made, by electrolytic deposition, free from carbon and from other metals. Even so made it apparently contains occluded gases. If ferrous oxalate be heated in a stream of hydrogen, it is reduced to metallic iron and if as low a temperature as possible is used the iron will take fire on exposure to the air (pyrophoric iron).

**Properties.**—Pure iron apparently exists in at least three allotropic modifications known as  $\alpha$  ferrite,  $\beta$  ferrite, and  $\gamma$  ferrite, the transition points of which are  $750^{\circ}$  and  $860^{\circ}$ . The changes from  $\gamma$  to  $\beta$  and from  $\beta$  to  $\alpha$  are both accompanied by evolution of heat. The same statement applies in a general way to steel, though the transition points both lie at or near  $720^{\circ}$ . When steel is heated white hot and allowed to cool it glows less brightly as it cools, until at about  $700^{\circ}$  it again brightens due to the heat liberated by the change to  $\alpha$  ferrite. This is known as "recalcescence" of steel. Fig. 134 shows the heating and cooling curves as given by Osmond.

Iron in the ordinary form, such as piano wire (99.8 per cent



iron), is a lustrous gray metal. It softens sufficiently for welding at about  $1000^{\circ}$  but does not melt until about  $1550^{\circ}$ . Its boiling point is near  $3000^{\circ}$  C. Its specific gravity is 7.84. It is malleable and ductile. It becomes "magnetic" when in the field of an electric current or in contact with a magnet. It is not attacked by dry oxygen or air, but in moist air rapidly rusts.

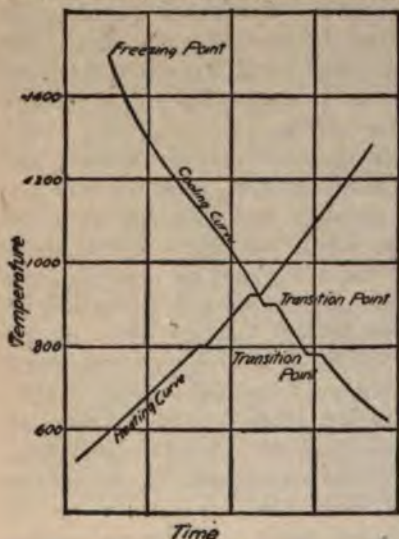


FIG. 134.

As ordinarily encountered its surface is protected by a film of magnetic oxide,  $\text{Fe}_3\text{O}_4$ , formed while the heated iron is in contact with air. The rusting in water is hastened by the presence of acids or of salts of acid reaction. It dissolves readily in acids, evolving hydrogen from the non-oxidizing acids. Heated with oxidizing acids, salts are formed and reduction products of the acids are evolved.

If iron be placed in strong nitric acid it fails to dissolve and is apparently wholly unaffected by the acid (see Passive Metals below). When iron is used as the anode of an electrolytic cell it dissolves according

to Faraday's law (*q.v.*), if the current density is not too great. At a definite current density in oxygen electrolytes, its surface brightens and oxygen is evolved and no further solution of iron takes place (see Passive Metals below).

Iron reacts with many metals to form alloys and forms definite compounds by direct addition with non-metals such as carbon, sulfur, phosphorus, etc. It is impossible to determine the boundary separating the two classes of substances and both will be discussed below under the headings, Cast Iron and Steel. Iron is a typical metal in its ordinary behavior and forms two series of salts, known as ferrous and ferric salts, in which it is bivalent and trivalent respectively. These salts are rather readily converted from the one to the other by oxidizing and reducing agents. In the ferric condition iron is less strongly basic than in the ferrous form and most ferric compounds are hydrolyzed in water

giving acid reactions with indicators. Under special conditions iron can be induced to exhibit a valence of six and in these forms is distinctly acidic. The specific heat of iron is 0.116, hence by Dulong and Petit's law its atomic weight should be approximately 55. By analysis of its oxides and from the composition of its volatile compounds the exact atomic weight is deduced as 55.85.

**Passive Metals.**—This extremely interesting phase of the behavior of metals deserves special discussion not alone because of its striking character but because so frequently erroneous statements concerning it appear.

When metals are placed in acid or are used as anodes they divide themselves roughly into classes: those which dissolve and those which do not. (The same dividing line does not however appear in the two cases.) The metals which dissolve in acids are sometimes termed base metals and those which do not are termed noble metals. When base metals are used as anodes in electrolytic cells the usual behavior is that they go into solution according to Faraday's rule, *i.e.*, 96,600 coulombs of electricity dissolve one gram equivalent of the metal. Under certain circumstances, however, these metals fail to dissolve. In such cases we are able to distinguish two types. In some cases metals become covered with a visible coating of insoluble material and are thus cut off from actual contact with the solvent. This, for example, occurs when cobalt is used as an anode in oxalic acid or oxalate solutions. Other cases occur in which no visible evidence of any coating appears but the metal ceases, wholly or partially, to dissolve. When in this condition, it is possible also to transfer them to solvents ordinarily capable of reacting with them and in many cases no reaction occurs. This condition of metals is referred to as the **passive state**. The phenomenon was first observed by James Keir in 1790 in the case of iron when dipped in concentrated nitric acid. Since that time numerous investigations have been directed toward the subject and a considerable number of explanations advanced. The explanation which seems most reasonable is a combination of the suggestions of Le Blanc (1905) and of Faraday (1836): that when iron is dipped in nitric acid or used as an anode in oxygen-bearing electrolytes, it becomes coated with a film of oxygen which adheres closely to the surface and effectively prevents contact with solution. The reason suggested by Le Blanc for the precipitation of oxygen when the metal is used as an anode is the



slow rate of ionization of iron which when sufficiently heavy electrical currents are used is not able to supply ions to carry the current. (See Jour. Am. Chem. Soc., Vol. 30, p. 1718, 1916.) In nitric acid, dichromates and chromates and in alkaline solutions, iron therefore cannot rust because protected by a film of oxygen. When hot solutions are used the protecting film is not always formed. Other metals which exhibit passivity are nickel, molybdenum, tungsten, and perhaps others. Contrary to the usual statements, cobalt shows no evidence of a truly passive state.

Chromium is passive in another sense in that with high current densities it dissolves apparently in the hexavalent form, instead of as ordinarily as a trivalent element.

**Cast Iron and Steel.**—When iron is melted in contact with carbon, as in the smelting process, carbon is dissolved to varying degrees, the maximum being about 4.5 per cent. Apparently when hot the carbon forms a compound with the iron, but when cooled slowly, as when molded in sand, the carbon separates out as graphite and the cooled metal is dark gray in color. If cooled suddenly, as when poured into iron molds, the carbon remains combined with the iron probably as cementite,  $\text{Fe}_3\text{C}$ , and the castings are white. Intermediate between the varieties is "mottled pig." The higher the percentage of carbon in pig iron the more extensively the graphite separates out. The pig iron also contains, as has been mentioned, varying proportions of silicon, sulfur, phosphorus, etc. The solubility of carbon in iron is greatly increased if manganese is present and "spiegeleisen" may contain as high as 7 per cent carbon.



FIG. 135.

Steel containing 0.4 to 0.6 per cent carbon is frequently called "medium" steel. Both steel and cast iron melt at lower temperatures than pure iron and the eutectic mixture appears to be that containing 4.3 per cent carbon which melts at 1130°. Figure 135 represents the freezing point curve.

Steel, primarily, is iron free from impurities except carbon, which gives to steel its superior hardness, tensile strength and "tempering" properties. "Hard" steels contain 0.5 to 1.0 per cent carbon and "soft" steels from 0.5 to 0.1 per cent.

When steel is melted and slowly cooled the changes which appear to take place are as follows: The molten steel consists of  $\gamma$  ferrite with carbon in solution as  $\text{Fe}_3\text{C}$ . As it cools, at or before  $1130^\circ$  (see curve), it solidifies to a solid solution of cementite in  $\gamma$  ferrite. On slowly cooling, the  $\gamma$  ferrite changes after  $860^\circ$  is reached to  $\beta$  ferrite and at  $670^\circ$  or below  $\alpha$  ferrite is formed. Untempered steel may be considered as  $\alpha$  ferrite mixed with iron carbide. If steel be suddenly cooled (quenched) the carbide has no opportunity to segregate from the ferrite and remains in solid solution. Also the speed of transformation of  $\gamma$  and of  $\beta$  to  $\alpha$  ferrite is reduced to infinite slowness. The result is varying degrees of hardness and brittleness known as "temper." The tempering of steel is thus an illustration of the law of transformation by steps (p. 542). The various components of quenched steel may be distinguished upon polished surfaces by means of the microscope, and microscopic examination of steel is becoming of increasing importance in technical work. Manganese, nickel, tungsten, etc., greatly retard the transformation of  $\gamma$  ferrite into  $\alpha$  ferrite and are consequently of value in the production of steels of great hardness and possessing other qualities desirable for special uses. The above explanation of the changes undergone in cooling steel are not universally accepted by steel men and have been the subject of very heated controversy.

**Uses of Iron.**—Pure iron is not used commercially and is too soft as well as too expensive for most purposes. Iron containing carbon, silicon, or other impurities, i.e., "pig iron," may be used for a great variety of purposes when its brittleness does not preclude its use. It is used to make a wide range of castings, hence is called cast iron. It is at times desirable to harden the surface of castings where wearing quality is desired, as in the rims of wheels, the moldboards of ploughs, etc. This is accomplished by casting in metal molds. The suddenly chilled metal retains carbon in solution and also probably remains largely as  $\gamma$  ferrite. The most extensive use of pig iron is of course in the manufacture of wrought iron and steel. The quantity usually produced is prodigious, being in 1913 approximately 80 million long tons of which about 32 million tons are accredited to the United States and nearly 14 million tons to one corporation, the United States Steel. The chief countries are the United States, Germany, and England in the order named. From this enormous quantity,



steels of all grades were produced in the same year to the amount of 75 million tons. Wrought iron is used for nails, horseshoes, plates, wire, etc., but relatively is not now so much used as formerly because mild steel has largely taken its place in materials where flexibility alone is required. For piano wire and for dynamo and other magnets and many similar purposes wrought iron is still very important. Mild steel is now used for sheet iron, in a bewildering variety of applications; for rails, ship construction, structural steel, etc. Hard steel is used for tools, cutlery, armor plate, guns, and countless other purposes for which it is adapted by reason of the varying degrees of tensile strength, hardness, and flexibility which may be provided by variation of the carbon content and the methods of treatment, hardening, annealing, and tempering.

**Special steels** are, as the name indicates, provided to meet certain special requirements: as tungsten steel for tools to be used at high temperatures, manganese steel for "burglar proof" safes, etc.

**Compounds. Halides.**—Iron forms by solution in hydrochloric acid ferrous chloride,  $\text{FeCl}_2$ , and hydrogen. It may be crystallized as a nearly white solid,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . It may be volatilized in anhydrous form and then appears to be  $\text{Fe}_2\text{Cl}_4$ . As the temperature at which the vapor density is determined is raised, the molecular weight decreases until it corresponds to the formula  $\text{FeCl}_2$ . It oxidizes readily to form ferric chloride  $\text{FeCl}_3$ . In moist air a basic salt is formed  $\text{Fe} \begin{smallmatrix} \text{OH} \\ \text{Cl}_2 \end{smallmatrix}$ .

Ferric chloride may be crystallized out of solution as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . In anhydrous form its vapor shows a molecular weight corresponding to the formula  $\text{Fe}_2\text{Cl}_6$ . It is reduced readily to ferrous chloride by reducing agents. The ready reduction of ferric to ferrous salts and the reversal by oxidation is common to all iron salts. Ferric chloride is highly hydrolyzed in aqueous solution and is hence strongly acid. Both ferrous and ferric ions are colorless in solution but due to hydrolysis ferric salts are highly colored, probably by reason of colloidal or dissolved ferric hydroxide. The truth of this statement is indicated by the increase of color when solutions are heated and by decrease when acid in excess is added. Of the other halide salts the only one of special interest is the iodide. Ferric iodide decomposes in solution giving ferrous iodide and iodine.

**Oxides and Hydroxides.** — Three oxides of iron are usually catalogued as such, *viz.*, ferrous oxide,  $\text{FeO}$ , magnetite,  $\text{Fe}_3\text{O}_4$ , and ferric oxide,  $\text{Fe}_2\text{O}_3$ . There are derivatives also of an oxide,  $\text{FeO}_3$ , although the oxide itself is unknown. Ferrous oxide is most readily formed by reduction of carbon dioxide with iron,  $\text{Fe} + \text{CO}_2 \rightarrow \text{FeO} + \text{CO}$ , a reaction which takes place in the furnace. It is also formed by reduction of ferric oxide by hydrogen if the reduction is accomplished at or about  $300^\circ$ . When exposed to the air it oxidizes spontaneously to ferric oxide and in finely divided form glows brightly from the heat produced. The corresponding hydroxide,  $\text{Fe}(\text{OH})_2$ , is formed by precipitation of ferrous salts by bases. It is white if no free oxygen has access to the solution. In presence of air it rapidly oxidizes and ultimately passes into ferric hydroxide. Intermediate between the two hydroxides there may be prepared, or occur in nature, more or less definite compounds, the green precipitate ordinarily observed being approximately  $\text{Fe}_3(\text{OH})_8$ . Ferrous hydroxide does not react with bases but is readily soluble in acids. It is itself soluble to an appreciable extent and its precipitation by ammonium hydroxide is therefore hindered by the presence of ammonium salts (see magnesium hydroxide). Ferric hydroxide is on the contrary an extremely insoluble hydroxide and precipitates as a jelly-like brown mass. When dried it dehydrates more or less completely, giving hydrated oxides and finally the oxide. These derivatives occur in many forms in nature as, limonite,  $\text{Fe}(\text{OH})_3$ ; goethite,  $\text{FeOOH}$ ; brown ore,  $\text{Fe}_4(\text{OH})_6\text{O}_3$ ; bog ore,  $\text{Fe}_2\text{O}(\text{OH})_4$ , etc., and as a completely dehydrated substance, hematite,  $\text{Fe}_2\text{O}_3$ . Ferric oxide,  $\text{Fe}_2\text{O}_3$ , may also be made by calcining the salts. In such soft form it is known as "rouge" and "venetian red" and is used as a pigment and variously otherwise. The hydroxide is not readily dissolved by bases but by fusion with basic oxides compounds may be formed, which may be con-

sidered to be derived from the meta-acid, *i.e.*, from  $\text{Fe} \begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$ .

These compounds also occur in nature, as, for example, franklinite,  $\text{Zn}(\text{FeO}_2)_2$ . Magnetite or lodestone,  $\text{Fe}_3\text{O}_4$ , is probably

such a salt, being derived from  $\text{Fe} \begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$  by neutralization with

ferrous oxide, *i.e.*, it is  $\text{Fe}(\text{FeO}_2)_2$ . It is also formed when ferric oxide is heated to  $1000^\circ$  or upward,  $3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{O}_2$  (*cf.*



effect of heat on manganese dioxide and lead peroxide). It is also formed when hot iron is hammered (hammer scale) and when iron reduces water vapor at high temperatures. When ferric oxide is treated with hydrogen peroxide no peroxide is formed but if fused with sodium peroxide, or if in suspension in concentrated potassium hydroxide solutions the hydroxide is treated with chlorine, purple or sometimes variously colored solutions are formed which contain alkali salts of ferric acid, *e.g.*,  $K_2FeO_4$ , which have been obtained in solid condition. These salts readily decompose and neither ferric acid itself nor the corresponding oxide have been isolated.

**Cyanides of Iron.**—When to salts of iron potassium cyanide is added, the precipitate first formed is apparently ferrous and ferric cyanides but with excess of the reagent, double salts are formed respectively  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ , known commercially as "yellow prussiate" and "red prussiate." The former, potassium ferrocyanide, is usually prepared by fusion of animal refuse, such as horn parings, blood, etc., with iron filings and potassium carbonate. It is a beautifully crystalline yellow salt,  $K_4Fe(CN)_6 \cdot 3H_2O$ , and in solution gives no evidence of the presence of iron as a positive ion. On the contrary with metallic ions it forms salts, many of them insoluble, by double decomposition in which the iron forms a part of the negative ion. Thus we have,  $K_4Fe(CN)_6 + 2CuSO_4 \rightarrow 2K_2SO_4 + Cu_2Fe(CN)_6$ . (Cf. p. 157.)

The potassium ferrocyanide solution if treated with chlorine or other good oxidizing agent turns red and by concentration produces crystals of the ferricyanide,  $2K_4Fe(CN)_6 + Cl_2 \rightarrow 2KCl + 2K_3Fe(CN)_6$ . This is known as "red prussiate." Like the ferrocyanide it also shows no evidence in solution of the presence of the iron as an ion. Indeed, from these salts the free acids,  $H_4Fe(CN)_6$  and  $H_3Fe(CN)_6$ , have been isolated, by treatment with hydrochloric acid. They also show no evidence of the presence of cyanide ions and the compounds are not even poisonous. Both types of salt are useful. The ferrocyanides besides being a source of cyanides (cf. p. 338) are gentle reducing agents. The ferricyanides are likewise, in alkaline solution, moderate oxidizing agents. Their chief interest lies in their insoluble salts, particularly those with iron itself. The treatment of the ferrocyanide with ferric salts gives a precipitate of "Prussian blue,"  $3K_4Fe(CN)_6 + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$ , while the ferricyanide with ferric salts gives a red color which is probably due to  $FeFe(CN)_6$  though no

such compound is isolated. Ferrous salts give with the ferrocyanides a white precipitate, quickly turning blue by oxidation, which is probably  $\text{FeK}_2\text{Fe}(\text{CN})_6$  or perhaps  $\text{Fe}_2\text{Fe}(\text{CN})_6$ . With the ferricyanides ferrous salts give a blue precipitate,  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ , known as Turnbull's blue. Both these blue compounds are used as pigments (*cf.* p. 568, "chrome green") and as laundry bluing. One case of special interest is the formation of **blue prints**. This and other like processes depend upon the fact that ferric salts are, in many cases, reduced to the ferrous condition on exposure to light. Thus, if paper which has been soaked in a mixture of ferric ammonium citrate and potassium ferricyanide is dried and exposed to light the ferric citrate is reduced to the ferrous salt. If the paper be now dipped in water the ferrous salt reacts with the ferricyanide to produce a blue precipitate. Where no light is admitted the mixed materials simply dissolve. Prussian blue is decomposed by alkalis and hence blue prints may be written upon, in white, with a dilute solution of sodium hydroxide.

**Sulfides of Iron.** — There are four sulfides of iron. Ferrous sulfide,  $\text{FeS}$ , is made either by heating iron and sulfur together (p. 12) or by passing hydrogen sulfide into alkaline solutions of either ferric or ferrous salts, or by addition of ammonium sulfide. It is insoluble in water but readily soluble in even very weak acids. It oxidizes readily, when moist, if exposed to the air, forming a basic sulfate and sulfur. Ferric sulfide,  $\text{Fe}_2\text{S}_3$ , cannot be formed in aqueous solution since it hydrolyzes in water and the hydrogen sulfide reduces the ferric to ferrous ions. Hence, ferric salts give ferrous sulfide with alkaline sulfides. It may be formed by heating iron and sulfur together in proper proportions at  $550^\circ$ , or by passing hydrogen sulfide over ferric oxide at  $100^\circ$ . This is the reaction used in the gas works for purification of gas. The reaction is reversed in the air and hence the oxide is regenerated.

The most common sulfide of iron is iron pyrites,  $\text{FeS}_2$  (fool's gold). It can be made artificially by gentle warming of iron with an excess of sulfur. The disulfide is extremely insoluble in water and for that reason, probably, rather than its stability, is not readily dissolved by acids. Hot hydrochloric acid and the oxidizing acids decompose it readily. When heated alone it decomposes, giving sulfur and "magnetic sulfide of iron,"  $\text{Fe}_3\text{S}_4$ , which is found in nature as pyrrhotite (*cf.* the oxide). In nature many minerals are found which may be regarded as iron pyrites in which other



metals more or less completely replace iron or other non-metals replace sulfur, such as  $\text{FeAsS}$ , arsenopyrite, etc. When roasted these sulfides are converted to iron oxide and sulfur dioxide and the decomposition is used to make the latter substance for use in the manufacture of sulfuric acid. The oxide still retains so much sulfur that it is seldom used for preparation of iron though some is employed under the name of "bulldog" in the preparation of wrought iron by puddling.

**Other Compounds.**—Of the remaining compounds of iron, numerous as they are, only ferrous sulfate and ferric acetate need special mention. The former, known as copperas,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (also known as green vitriol), is readily formed by solution of iron with sulfuric acid. Commercially it is also prepared by allowing iron pyrites (usually marcasite) to "weather," i.e., oxidize in the air, and leaching it with water. The solution contains also ferric sulfate, which is reduced by scrap iron, and the solution evaporated until the green crystals form. The crystals are efflorescent in dry but not in moist air. By air or other oxidizing agents it is converted to a basic ferric sulfate. The substance in solution unites with nitric oxide (the "ring" test for nitric acid) to form an unstable complex usually considered as  $\text{Fe}(\text{NO})\text{SO}_4$  which, however, ionizes apparently as  $\text{FeNO}^{\circ\circ}$  and  $\text{SO}_4^{\circ\circ}$ . It forms a double salt which is very stable with ammonium sulfate,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , not isomorphous with the alums. Ferrous sulfate is used as a mordant, as a reducing agent, and in the manufacture of ink. The last reaction is due to the formation of ferrous tannate. (See ink formulæ.) Ferric acetate,  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ , is a soluble salt formed by double decomposition with the acetates and ferric salts. It forms a blood red solution which on boiling hydrolyzes to a basic insoluble salt,  $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$ .

#### NICKEL AND COBALT

These two metals with atomic weights so nearly the same, Ni, 58.68, and Co, 58.97, are more nearly twin elements than any other of the elements, at least of those with atomic weights less than 140. They will therefore be discussed together.

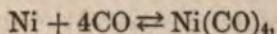
**Occurrence.**—The two elements are nearly always associated in their ores and these are called nickel or cobalt ores, as one or the

other metal predominates in quantity. Nickel is somewhat the more abundant in general. Both occur as alloys to some extent in minerals. The ore **smaltite** is  $\text{CoAs}_2$ , **kupfernickel**, or **nicolite**, is  $\text{NiAs}_2$ , **nickel glance** is  $\text{NiAsS}$ , and **cobalt glance** is  $\text{CoAsS}$ . **Millerite** is the sulfide  $(\text{NiCo})\text{S}$ . The most important nickel ore is probably a nickel magnesium silicate  $(\text{NiMg})\text{H}_2\text{SiO}_4$ , **garnierite**, found chiefly in New Caledonia.

**History.** — The name cobalt is derived from the German **Kobald**, or earth dwarf, which was the evil spirit of mines. Nickel seems to be derived from the term **kupfer-nickel**, or false copper, which was used to describe minerals supposed to be copper ores but from which copper could not be obtained. The discovery of the elements is ascribed to Brandt, cobalt, in 1735, and Cronstedt, nickel, in 1751, although the term cobalt had been used for many years to describe the minerals used for coloring glass blue and for many centuries Chinese coins were alloys of copper and of nickel.

**Preparation.** — Until recently, cobalt ores were not treated to obtain the metal. The general method is to convert the metal to the chloride by treatment with hydrochloric acid, remove the second group metals (p. 398) with hydrogen sulfide, oxidize the solution with chlorine, and precipitate the iron with chalk. The cobaltic oxide is then precipitated by addition of chlorine to the neutral solution. The metal may be obtained by reduction of the oxide by hydrogen.

Nickel is ordinarily prepared by methods which are modifications of those used for copper. Since copper is ordinarily also present the alloy formed is separated as in the electrolytic refining of copper (*q.v.*). The separation of cobalt from nickel is based upon the formation with nickel of a volatile compound, nickel-carbonyl,  $\text{Ni}(\text{CO})_4$  (*cf.* p. 334), from which the nickel can be recovered by heating. The reaction is an interesting case of a reversible reaction,



which goes in the direction  $\rightarrow$  with an excess of carbon monoxide (at 15 atmospheres) and reverses when the excess of monoxide is removed. Both metals are most readily prepared by the Goldschmidt process.



**Properties.** — Nickel and cobalt are both hard white metals, both are malleable and ductile, both are magnetic but less so than iron. Their specific gravity is practically the same, nickel is given as 8.8, cobalt as 8.7. Their melting points are nearly the same, cobalt  $1500^{\circ}$  and nickel  $1450^{\circ}$ . Both are corroded very slowly by moist air and react with steam to produce the monoxide, a contrast with iron (p. 54). Both are soluble in dilute acids and both become passive (p. 601) in nitric acid, but while nickel is readily rendered passive as an anode cobalt is not. Both form two series of salts, a bivalent series and a trivalent one, but while bivalent soluble nickel salts are green and cobaltous salts in solution are pink the colors appear to reverse when the trivalent salts are formed.

**Uses and Alloys.** — As a metal cobalt has found few special uses, but recently it has been found very valuable as a component of a steel for the manufacture of cutlery. This alloy is 75 per cent cobalt and 25 per cent chromium. Nickel, on the other hand, has been used extensively for plating other less durable metals and for decorative purposes. Its alloys, as German silver and coins, are extensively used (see appendix). Nickel steel for armor plate and similar purposes has great value. "Invar," used for standard measures, and "platinite," used for making wire glass and in lieu of platinum for incandescent bulbs, are nickel steels containing about 36 per cent and 42 per cent of nickel respectively. The latter has nearly the same coefficient of expansion as glass. Monel metal, a "brass," composed of nickel and copper, is less readily tarnished than brass or bronze and is used in their stead for certain purposes.

**Compounds.** — The bivalent salts of both cobalt and nickel are more common than the trivalent forms. The hydroxides are precipitated from alkaline solutions and the nickelous hydroxide is stable but the cobaltous hydroxide, like that of iron, slowly oxidizes on exposure to air. Cobaltous chloride treated with bases precipitates a blue basic salt,  $\text{Co}(\text{OH})\text{Cl}$ , which is converted to the hydroxide on boiling. Both hydroxides change to the corresponding oxides when heated in the absence of air and both oxidize to the "ic" forms when heated in the air. The salts of neither metal are precipitated by ammonium hydroxide, since both form complex ammonia ions. (Cf. copper.) Ammoniacal solutions of

cobalt salts absorb oxygen from the air and form cobalt ammines. These complex and very interesting salts play an important part in Werner's hypothesis (*q.v.*). Both metals form many complex salts and the double sulfate,  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is the most important compound of nickel because of its use in nickel plating baths. The cyanides of both metals dissolve in an excess of the alkali cyanides, forming double cyanides.

The double cyanide of cobalt,  $\text{K}_2\text{Co}(\text{CN})_4$ , is oxidized to the cobaltic cyanide,  $\text{K}_3\text{Co}(\text{CN})_6$ , with bromine or chlorine. The product is stable in alkaline solution. Nickel forms a similar double cyanide, if oxidized, which is decomposed by bases forming nickelic hydroxide,  $\text{Ni}(\text{OH})_2$ . A similar double salt, the double nitrite, is formed by both metals. The double nitrite of cobalt and potassium,  $\text{K}_2\text{Co}(\text{NO}_2)_6$ , is quite insoluble in water, while that of nickel is soluble. Both metals form oxides analogous to magnetite, *viz.*,  $\text{Co}_3\text{O}_4$  and  $\text{Ni}_3\text{O}_4$ . Neither metal forms the true peroxides but a most remarkable set of changes occur if their "ous" salts are treated with hydrogen peroxide in the presence of potassium hydrogen carbonate solution. With cobalt a **vivid green** solution is formed, with nickel at  $0^\circ$  a **faint pink** solution is produced. The compounds forming these have never been isolated. They are presumed to be  $\text{KCo}(\text{CO}_3)_2$  and  $\text{KNi}(\text{CO}_3)_2$ , but this is uncertain (*Jour. Am. Chem. Soc.*, Vol. 30, p. 1732). The beads formed by cobalt with microcosmic salt are blue both in the oxidizing and reducing flame. Nickel beads are reddish brown in the oxidizing flame. Cobalt glass made from cobalt oxide, potassium salts, and silica is known as smalt and is an important blue pigment. **Thenard's blue** is made by heating cobalt salts with alumina. It is probably  $\text{Co}(\text{AlO}_2)_2$ .

#### THE PLATINUM METALS

**Occurrence.**—The two remaining triad groups are together known as the platinum metals because they occur almost exclusively in the native state, alloyed together, as nuggets or in fine grains. Of these the platinum ranges from two-thirds of the alloy upwards to nearly pure platinum. Gold is nearly always associated with this crude alloy. Nearly the whole supply of all the metals and their salts are derived from this source; though very rare minerals having isolated members of the group are known. Also from certain Brazilian gold ores and from the copper-nickel-



cobalt ores of Sudbury and from gold refineries some of these metals are recovered. The chief sources are in the Ural mountains.

**History.**—Platinum was first discovered in South America by the Spaniards and named "platina," the diminutive of *plata*, silver. It was first brought to Europe in 1740 and described by Watson in 1748. Its importation to Europe was forbidden by the Spaniards in order to prevent its use for adulteration of gold. In 1788, however, the Spanish government bought it, perhaps to "debase" its coinage, at about two dollars per pound. Its price in 1916 was three dollars per gram. Tennant in 1802 isolated from the crude platinum osmium and iridium and named them. (The former is from  $\delta\sigma\mu\eta$  = a smell, the latter from  $\text{iris}$  = a rainbow, because of the most striking physical characters of the compounds (cf. p. 114).) In 1804, Wollaston, in an investigation designed to discover uses for these metals (!) discovered rhodium and palladium. The former was named from  $\rho\acute{o}\delta\omicron\nu$  = a rose, from the color of its salts, and the latter after the planet Pallas (discovered in 1802). In 1845, Claus isolated ruthenium and named it (from Ruthen, an ancient term for Russia).

**Preparation.**—Since the platinum elements are so exclusively found native and alloyed not only with each other but also with gold and other elements as well, the separation and isolation is a fairly complicated series of processes, the details of which are not essential to our present purpose. The actual methods employed commercially are held as "trade secrets." The metals are collected from the sands by concentration and by washing, the amalgamation process (cf. Gold, p. 436) being used for final extraction. After evaporation of the mercury the residue is treated with aqua regia. The insoluble residue is chiefly an alloy of osmium-iridium. Osmium and ruthenium form volatile oxides (cf. below) which are removed by distillation. The platinum with some iridium is removed from the solution by precipitation with ammonium chloride. The double chloride is decomposed by heat,  $(\text{NH}_4)_2\text{PtCl}_6 \rightarrow 2\text{NH}_3 + 2\text{HCl} + \text{Pt} + 2\text{Cl}_2$ . The palladium and rhodium remain in the mother liquor.

**Ruthenium, Ru**, 101.7, forms four oxides,  $\text{RuO}$ ,  $\text{Ru}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{RuO}_4$ . The tetroxide is a volatile compound with an odor resembling that of ozone. It may be readily reduced to the metal by various reducing agents, and if heated under pressure is reduced to the dioxide,  $\text{RuO}_2$ . There is no oxide corresponding

to  $\text{RuO}_2$  or  $\text{Ru}_2\text{O}_7$ ; but the salts potassium ruthenate,  $\text{K}_2\text{RuO}_4$ , and potassium perruthenate,  $\text{KRuO}_4$ , are formed. Their solutions are orange-red and green, respectively. The chlorides,  $\text{RuCl}_2$ ,  $\text{RuCl}_3$ , and  $\text{RuCl}_4$ , are known and also the double chlorides (*cf.* p. 521). The metal itself is gray in color, with a specific gravity of 12.3 and a melting point of about  $2300^\circ$ . It is obtained in very small quantities and finds no uses at present.

**Rhodium, Rh**, 102.9, forms three oxides,  $\text{RhO}$ ,  $\text{Rh}_2\text{O}_3$ , and  $\text{RhO}_2$ , and two chlorides,  $\text{RhCl}_2$  and  $\text{RhCl}_3$ . The latter forms double salts readily. It also forms ammonia derivatives like those of cobalt and platinum, *e.g.*, roseorhodium chloride,  $\text{Rh}(\text{NH}_3)_5\text{H}_3\text{OCl}_3$  (*cf.* p. 618). It is a hard white metal with a specific gravity of 12.6 and a melting point of about  $1900^\circ$ . It is used somewhat to tip gold pens.

**Palladium, Pd**, 106.7, is sometimes found associated with silver ores as well as always with platinum. It is much more abundant than the other members of its triad. It forms but two oxides,  $\text{PdO}$  and  $\text{PdO}_2$ , and two chlorides,  $\text{PdCl}_2$  and  $\text{PdCl}_4$ . The latter is known only in solution but forms a double salt,  $\text{K}_2\text{PdCl}_6$ , insoluble in water. The dichloride is formed by dissolving spongy palladium in hydrochloric acid. When the chlorides are reduced the finely divided palladium is obtained, known as "spongy palladium." Complex ammonia derivatives of palladium are known (*cf.* p. 615). The metal is similar in appearance to platinum. It is malleable and ductile. Its specific gravity is 11.9 and its melting point is  $1550^\circ$ . It is said to be used as an adulterant of platinum. Its most remarkable property is its absorptive power for hydrogen; 1 cc. of the metal in the form of foil will absorb from 550 to 800 times its own volume of the gas. As an electrode in spongy form it is said to absorb as much as 900 to 1000 times its own volume of the gas. The nature of this relation is unknown. It appears to be a solid solution. The hydrogen is more active than ordinary hydrogen, *e.g.*, it reduces copper salts to metallic copper and it oxidizes rapidly on contact with air. The finely divided metal, therefore, finds use in gas analysis, to estimate hydrogen, in automatic gas lighting devices, and as a catalyzer in various reactions. (See New Alloys to Replace Platinum, *Jour. Ind. and Eng. Chem.*, 9, 590.)

**Osmium, Os**, 190.9, forms four oxides,  $\text{OsO}$ ,  $\text{Os}_2\text{O}_3$ ,  $\text{OsO}_2$ , and  $\text{OsO}_4$ . The chlorides are  $\text{OsCl}_2$ ,  $\text{OsCl}_3$ , and  $\text{OsCl}_4$ . It also forms osmates, as  $\text{K}_2\text{OsO}_4$ . The oxide,  $\text{OsO}_4$ , is a volatile white solid, the vapor of which has a very disagreeable smell resembling that of chlorine. It is known as "osmic acid," though, while soluble in water, it has no acid properties. It is used for staining and hardening purposes in histology. It is used as a catalytic agent, particularly in the synthesis of ammonia (*cf.* p. 264). The metal is iron gray and remarkable as the densest of known materials, specific gravity, 22.5. It is also very infusible, melting point  $2700^\circ$ . It is used as an alloy with platinum for connecting wires in incandescent lamps, and, but for the superiority of tungsten and tantalum, could be used for filaments. It is also a constituent of the alloys used for gold pen nibs. Its



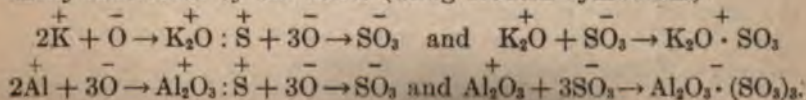
presence in platinum crucibles and dishes is very unpleasant, though not infrequent, because by heating in air the volatile oxide is formed and the vessels lose weight slightly after each heating.

**Iridium, Ir**, 193.1, forms two oxides,  $\text{Ir}_2\text{O}_3$  and  $\text{IrO}_2$ , and three chlorides,  $\text{IrCl}_3$ ,  $\text{IrCl}_3 \cdot 5\text{H}_2\text{O}$ , and  $\text{IrCl}_4$ . The chlorides form double salts of the type  $\text{K}_2\text{IrCl}_6$ . The metal resembles platinum in appearance, has a specific gravity of 22.4 and a melting point of about 2300°. Its alloy with osmium "iridosmine" is used for gold pen points. The metal is frequently present in platinum vessels in which it is an advantage since it renders them harder. The various standards of measure and of weight at Sèvres, near Paris, are of this type.

**Platinum, Pt**, 195.2, is far the most important metal of its group. It forms two oxides,  $\text{PtO}$  and  $\text{PtO}_2$ , and two chlorides,  $\text{PtCl}_2$  and  $\text{PtCl}_4$ , both of which form double chlorides readily. Of these double chlorides those with hydrochloric acid are known as chlorplatinous acid,  $\text{H}_2\text{PtCl}_4$ , and chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ . The salts of these acids with ammonium and potassium are insoluble in water and are extensively used in analytical chemistry in spite of their enormous cost. Platinum chlorides form a long series of ammonia derivatives, known as ammines. These compounds with those of cobalt and others of similar type led Werner to his view of the stereostructure of inorganic compounds, a view so comprehensive that it is given separate treatment (see p. 615). While platinum salts are valuable as reagents the great utility of platinum is in metallic form. The metal has a specific gravity of 21.4 and a melting point of 1750°. It is unaffected by moist or dry air or by heating in the air, though it may be melted by the oxyhydrogen blow-pipe. It is also unaffected by acids of any sort, though dissolved by aqua regia. It is also an extremely efficient catalytic agent, probably by reason of its powers of occlusion (cf. p. 61 and p. 232). It may be prepared either in a malleable, ductile, coherent form, or as a black powder. Its stability in the air and its physical properties, as well as its high cost, make it an extensively used material in the manufacture of jewelry, especially for chains, bracelets, jewel settings, etc. It is unfortunate that this is the case, as such uses limit the supply for scientific purposes, already insufficient. Another unfortunate application is as a "toning" material in portraiture by photography (cf. p. 449). This is simply a waste. The metal is very extensively used in the form of wire for sealing through glass for electrical connections, since its heat coefficient is nearly that

of glass. This makes it nearly indispensable in the manufacture of X-ray apparatus, incandescent lamp bulbs, explosive bulbs, eudiometers, etc. Its resistance to the electric current is fairly large at ordinary temperatures and decreases uniformly with fall of temperature. It is therefore used for resistance wires and for the construction of both low and high temperature thermometers. Its most valuable application, at least to the chemist, is in the form of wire, crucibles, dishes, combustion tubes, electrodes, etc., for use in chemical laboratories. These uses are so varied that it is a query how we could do without it, but its increasing cost is a constant source of anxiety to those who purvey the laboratory supplies. It is a mistake, however, to suppose it an inactive material under all circumstances and platinum apparatus is peculiarly susceptible to damage by the uninitiated. It is dissolved by aqua regia and indeed is corroded by any of the free halogens and nothing capable of giving rise to these substances should be used in platinum apparatus. It is also dissolved by alkalis and particularly when oxidizing agents are also present. It may be used for fusion with sodium carbonate, but even with this, with oxidizing agents, there is some corrosion. With many metals and metalloids it forms easily fusible alloys and since it is permeable by hydrogen, easily reducible substances such as lead, phosphorus, arsenic, and antimony compounds heated in platinum vessels spell ruin for the vessels since by reduction these form alloys and at the temperature of the burner these alloys melt. Finally, platinum heated with carbon slowly forms a carbide which is brittle and hence if platinum is heated in a smoky flame it gradually hardens and then may crack when subjected to any sudden blow. Platinum ware should therefore be treated with care and discretion. (See *The Platinum Situation*, Jour. Ind. and Eng. Chem., 9, 544, 1917.)

**Werner's Hypothesis.**—The dualistic view of the composition of compounds, known as Berzelius' Electro Chemical Theory (1813), assumed every chemical change as essentially electrical (p. 170), and that when electrically charged atoms unite a residual polarity of the compound remained which enabled it to unite with a group similarly charged, though of opposite polarity. This view is ordinarily illustrated by the series (using modern symbolism):





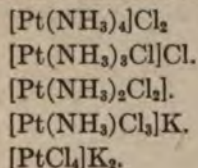
These two salts being oppositely charged were assumed to be capable of uniting:  $K_2O\overset{+}{SO_3} + Al_2\overset{-}{O_3} \cdot (SO_3)_3 \rightarrow K_2O \cdot SO_3 \cdot Al_2O_3(\overset{+}{SO_3})_3$ . This complex was assumed to be able to unite with water ( $H_2O$ ) to form alum, which was expressed,  $K_2O \cdot SO_3 - Al_2O_3(SO_3)_3 \cdot 24H_2O$ , or as written at present,  $KAl(SO_4)_2 \cdot 12H_2O$ . Coincident with the rapid development of organic chemistry the relations of the compounds produced could not be brought to harmonize with the dualistic view and after many years a view known as the theory of valency took its place (1856). The story of the evolution of valency, while very interesting, is too long to be introduced in this connection. (See Schorlemmers' *Rise and Development of Organic Chemistry*, or Pattison-Muir's *Chemical Theories and Laws*.) This latter view, which for many years has been, and still is, the prevailing view, regards each atom of an element as the seat of certain attractive forces of a numerical character which are considered fundamental properties of the atoms. There were two variants of this view. One, that of Kekule, regarded the valency of the atoms as invariable. The other regarded the atoms as possessing a maximum valency which in given cases might not manifest itself. It is the latter view which may be considered as the dominant one at present and upon which the preceding discussions have been based. Thus the periodic groups show certain maximum valencies which correspond to their group numbers. In each group, however, lower valency is operative in given cases. (Cf. structural formulæ of nitrogen compounds, p. 295.) While this conception of valency is satisfactory in general and provides a general basis of coördination of facts, it must be confessed that there are a number of facts for which it does not make provision and these include the groups of compounds such as the alums, vitriols, hydrates, double salts, and the ammino-compounds of cobalt, platinum, chromium, etc. Such of these as were known at the time were coördinated by the dualistic theory. In an attempt to satisfactorily account for the existence of these compounds Werner (1893 *et seq.*) has been led to a view of valency which while perhaps, and probably, not in its final form, ought to be presented in any survey of the chemical field. Contrary to the practice with all the hypotheses so far presented in this discussion we shall, for the sake of brevity, present without argument the assumptions made and then show how they apply to the above types of compounds. Werner assumes that besides the valency of the type

just discussed each element possesses a residual valency (corresponding to Berzelius' residual polarity) through which the compounds of the elements are enabled to unite to form complex compounds, *i.e.*, he recognizes the ordinary valency as the expression of the numerical combining value of an atomic weight of an element expressed in terms of the number of combining weights of hydrogen or its equivalent with which it can unite. The residual valency represents manifestations of chemical affinity which enable molecules to react, as radicals react, but differing from radicals in being able to lead independent existences. This residual valency has a limit for each kind of atoms and the sum of the ordinary valence and secondary valence he proposed to call the **coördination number** of the element. He recognizes three different coördination number groups, four, six, and eight, and because of the frequency of the occurrence of compounds where the coördination number of some one of the elements is six and is independent of the nature of the associated molecules, he is inclined to believe that space, rather than affinity relations, govern. He hence suggests space formulæ (stereo-formulæ) for compounds of the inorganic type, just as we have long recognized space relations in organic chemistry (see Organic Chemistry — van't Hoff and Le Bel's Theory). The space relations are, however, somewhat different from those arrived at from the study of organic compounds. In those compounds where the coördination number is four he assumes a space relationship in a plane and where the coördination number is six he assumes an octahedral structure of which examples will be given subsequently. The elements directly attached to a given central atom are indicated within brackets (the inner sphere) and those not directly attached are indicated outside the bracket (the outer sphere). The simplest case may be illustrated as follows: Nitrogen in ammonia is assumed to have an unsaturated secondary valency. Its coördination number is four and its formation of ammonium chloride with hydrochloric acid is indicated by  $\text{NH}_3 + \text{HCl} \rightarrow \text{H}_3\text{N}^+\text{H}-\text{Cl}$ . There seems to be no difference between any of the four atoms of hydrogen in ammonium chloride and consequently the chlorine is linked to the molecule,  $\text{NH}_4$ , by an affinity, or equilibrium, distributed over the whole group. This is indicated by the formula  $\left[ \begin{array}{c} \text{H} \diagup \text{N} \diagdown \text{H} \\ \text{H} \end{array} \right] - \text{Cl}$ . It now remains to justify to some extent this hypothesis which seems at first bizarre. The chlorides of platinum when treated with

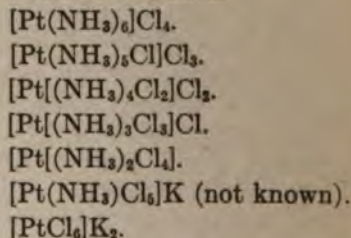


ammonia behave in a very interesting manner. Platinic chloride in solution treated with ammonia, and boiled, gives a green precipitate,  $\text{PtCl}_2 \cdot 4\text{NH}_3 - \text{H}_2\text{O}$  (Magnus' salt), and from the solution can be obtained a compound with the composition  $\text{PtCl}_2 \cdot 2\text{NH}_3$ . Both when treated with chlorine give a compound  $\text{PtCl}_4 \cdot 2\text{NH}_3$ . Such compounds are called **ammino-salts**. These may be considered as the typical members of two series of platinum compounds which have been prepared and for which our ordinary valence conceptions cannot account. Werner represents their composition as follows:

## Platinous Derivatives



## Platinic Derivatives



The physical and chemical behavior of these compounds accords in a marvelous manner with these formulations. According to Werner's assumption those portions of the compounds within the brackets (the inner sphere) act as a unit and this unit has a valence which is equal to the normal valence of the central atom, if a metal, less the number of acidic valences within the bracket. Accordingly, then, the compound  $[\text{PtCl}_4(\text{NH}_3)_2]$  has no valence, while  $[\text{PtCl}_2(\text{NH}_3)_4]$  should have a positive valence of two, while the complex  $[\text{PtCl}_6]$  should have a negative valence of two. These relations are shown in the above table. Moreover, the solutions of  $[\text{PtCl}_4(\text{NH}_3)_2]$  and of all others non-valent, according to the hypothesis, are non-conductors of the electric current, while those of the type  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$ , etc., and  $[\text{PtCl}_6]\text{K}_2$  are conductors. In the latter type potassium goes to the cathode during electrolysis; in the former the complex is the cation. Moreover, in such compounds as  $[\text{PtCl}_4(\text{NH}_3)_2]$  the chlorine is not present in solution in ionic form and does not precipitate with silver nitrate (see also cobalt ammines). More strikingly confirmative of the hypothesis is the fact that isomers are possible according to Werner's view and many of these have been isolated. Thus, there have been isolated two compounds of the type

$[\text{PtCl}_2(\text{NH}_3)_2]$  and two of the type  $[\text{PtCl}_4(\text{NH}_3)_2]$ . These are represented by space formulæ as follows:

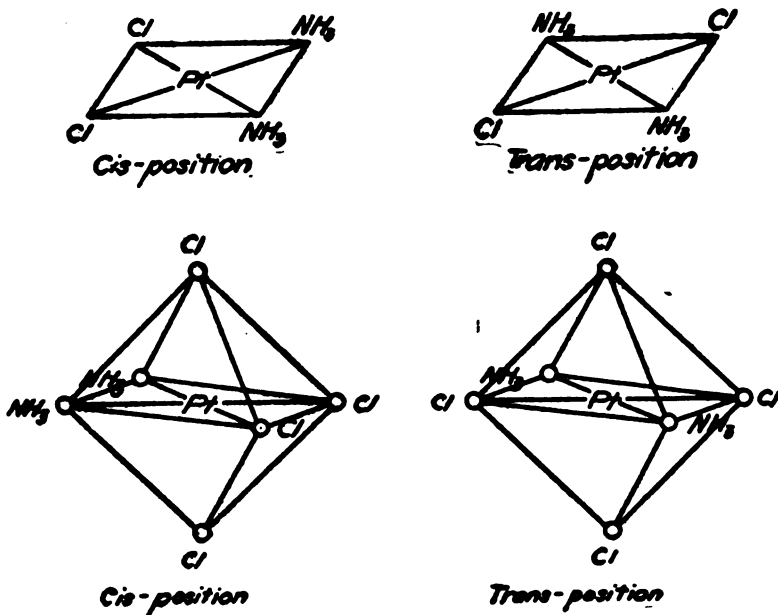


FIG. 136.

These space formulæ are not identical and by analogy with the *cis* and *trans* compounds of organic chemistry may be assumed to represent compounds of different types. Moreover, the ammonia groups of the above groups of compounds may be replaced by water or alcohol, etc. The number of derivatives is therefore very great and many have been prepared. In an exactly similar manner the hosts of complex ammines of the cobalt type which have been prepared may be accounted for. We have the following possibilities:





When we consider that the ammonia in these compounds may be replaced by Br, I,  $\text{NO}_2$ ,  $\text{NO}_3$ , CN,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , etc., we realize what an enormous number of compounds are possible. We must have consideration, even admiration, for any hypothesis capable of dealing with them. Hundreds of these compounds have actually been made. Indeed, we may consider potassium cobaltic cyanide and potassium cobaltic nitrite of this type, viz.,  $[\text{Co}(\text{CN})_6]\text{K}_3$  and  $[\text{Co}(\text{NO}_2)_6]\text{K}_3$ . In a similar manner the ammino derivatives of silver, copper, cadmium, and chromium fall into orderly classification.

It is possible to extend Werner's conception to the hydrates and alcoholates also. Thus, magnesium chloride crystals,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , he considers  $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$  and similarly for other hexahydrates. For the vitriols,  $\text{MSO}_4 \cdot 7\text{H}_2\text{O}$ , he considers one molecule of water a part, not of the nucleus, but of the acid, a conception in accord with the hydrated acid structure (cf. p. 237). Thus,  $[\text{Zn}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ . In the case of copper sulfate we have  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ . It should be repeated that the hypothesis of Werner is yet in the making. For fuller information the student should seek Werner's book. (*Neuere Auschauungen auf dem Gebiete der Anorganischen Chemie*, 1905.)

## CHAPTER XXXVI

### ATOMIC STRUCTURE AND THE PERIODIC LAW

**Inorganic Evolution.** — We have seen that the current view of the cause of radioactivity is a decomposition of the atoms of certain elements. This may be called the **Devolution of the Elements**. The converse of this is the theory of inorganic evolution. As early as 1815 Prout suggested that since so many of the elements have atomic weights which are a multiple by a whole number of that of hydrogen it may be that the atoms of other elements are made up of hydrogen, *i.e.*, that hydrogen may be the primordial matter, the *πρῶτη ὕλη* of the ancients. This idea was eagerly adopted at the time but due largely to the exact atomic weight work of the great Belgian chemist, Stas (1860–1865) the hypothesis was finally rejected. In one form or another the fundamental idea keeps reappearing in various forms. That this is true is perhaps due to such points as are here cited.

1. The atomic weights are nearly whole multiples of the weight of hydrogen. Harkins has pointed out (Jour. Am. Chem. Soc., Vol. XXXVII, p. 1370) that of the first twenty-one elements the average deviation from whole numbers is 0.21 and if four of these (Be, Mg, Si, and Cl) are left out the deviation of the remainder is but 0.05. Such a situation is not probable on the basis of chance. There must be some reason.

2. The elements have family relationships such as have been repeatedly pointed out and which form the basis of the periodic systems and moreover related elements are nearly always found associated in nature (*cf.* occurrence of cobalt, nickel, etc.).

3. The spectra of the elements are regarded as an atomic property (*cf.* p. 443), yet the following facts concerning the spectra seem to be definitely ascertained. (a) The spectral lines can be arranged in groups and elements of similar chemical types show similar groups of lines. In each periodic group there exists nearly the same relation between the wave lengths of the series of lines but



the higher the atomic weight in each group the set of lines is the nearer the red end of the spectrum. It has even been found possible to determine atomic weights on this basis. It is assumed, therefore, that each group of elements is made up of similar complexes.

(b) The spectrum of a given element is not always the same when it is examined by the "flame method," the "arc" method, and by electrical discharge through attenuated gases. Thus the flame spectrum of iron at relatively low temperature consists of but few lines. At higher temperature the "arc spectrum" consists of two thousand lines and at still higher temperatures, *i.e.*, at the temperature of the hot stars, it is said again to consist of but a few lines. In the highly attenuated gases the spectra disappear and we get the X-ray or electron production.

(c) The spectral lines when examined in the magnetic field are separated into groups of lines, pairs, triplets, etc., the Zeeman effect (1897), which was discovered after it had been foretold by Lorentz on the assumption of corpuscular rotation (1895).

(d) The spectra of nebulae consist of only a very few lines and these nebulae are supposed by astronomers to be the "star stuff" of which the older stars are formed by aggregation. Moreover, it is possible, by the use of the instrument known as the bolometer, to estimate the temperature of the stars. The nebulae appear to be the hottest form of heavenly body and as cooler stars are examined the number of spectral lines increase and the order of their appearance is approximately the order of the atomic weight of the terrestrial elements showing the same spectra. Only the cooler stars show the spectra of elements as complex as carbon. On the basis of a part of this evidence Lockyer had, as early as 1873, reached the conclusion that **chemical atoms have grown during the cooling of the stars from ultra atomic gas**, and further, that in the hottest stars there exist proto elements. This idea has been of recent years elaborated by Nicholson (1913, 1914) who, from the study of the spectra of the nebulae, very hot stars, and the corona of the sun, has reached the conclusion, based on mathematical calculations on the assumption of charged electrons, that terrestrial elements are evolution products of simple ring systems consisting of positive nuclei and negative electrons. (*Vide* Nicholson, *Phil. Mag.* 27, p. 541, and 28, p. 90.)

4. The most far-reaching set of facts tending to keep the composition of the atom in the minds of scientists is, of course, the

marvelous transformations which have been studied consequent upon the discovery of the X-ray and of radioactivity. (*Cf.* p. 578 *et seq.*)

On the basis, therefore, of these facts and hypotheses Harkins and Wilson (*Jour. Am. Chem. Soc.*, Vol. XXXVII, pp. 1367 and 1383) have recently advanced the rather startling conclusion that not only are the elements synthetic products of hydrogen atoms, but that all the elements belong to two types, called even and odd types, but that the variations from unit multiples of the atomic weights are due to **loss of weight** consequent upon the condensation of the electrons of the hydrogen atoms. This variation of **mass** is calculated to be 0.77 per cent in the formation of helium from the hydrogen complex. Succeeding members of the series of atoms are supposed to consist of hydrogen and helium atoms as indicated in the following table:

Group.	0	1	2	3	4	5	6	7	8
Element.....	He	Li	Be	B	C	N	O	F	....
Complex.....	H <sub>2</sub>	He+H <sub>2</sub>	2H <sub>2</sub> +H	2He+H <sub>2</sub>	3He	3He+H <sub>2</sub>	4He	4He+H <sub>2</sub>	....
Atomic weight....	4	6.94	9.1	11	12	14.01	16.00	19.00	....
Element.....	Ne	Na	Mg	Al	Si	P	S	Cl	....
Complex.....	5He	5He+H <sub>2</sub>	6He	6He+H <sub>2</sub>	7He	7He+H <sub>2</sub>	8He	8He+H <sub>2</sub>	....
Atomic weight....	20	23	24.32	27.1	28.3	31.02	32	35.46	....
Element.....	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Complex.....	10He	9He+H <sub>2</sub>	10He	11He	12He	12He+H <sub>2</sub>	13He	13He+H <sub>2</sub>	14He
Atomic weight....	39.9	39.1	40.07	44.1	48	51	52	54.93	55.84

There are certain difficulties with this hypothesis in that it does not carry through the whole series of elements so satisfactorily as in the elements cited above. Taken, however, in conjunction with the rather definitely established existence of isotopic elements (p. 584) these difficulties may be resolved. Based upon it, however, we have a periodic system which has undoubted utility (p. 626 *et seq.*). Whatever the ultimate fate of this sublimated form of the hypothesis of Prout the situation seems to be clearly developed that we have in the atoms of the elements, if they have material existence at all, not indivisible units of matter, as assumed by Dalton, but systems consisting of very complex combinations of charged bodies (whether wholly negative or partly positive and partly negative may not be definitely stated). These systems are in certain cases not stable but are decomposing at a rate unaf-



fectured by known means. The reverse process appears to be going on in the heavenly bodies. Human means at present are unable to affect either process. It is a reversible process beyond our present control. It may be said, then, that science makes use of the conception of the following imaginary bodies: molecules, atoms, electrons, and positive nuclei. (It may be remarked that the probability of the real existence of these bodies is in the order above given.)

**Size of Molecules, Atoms, Electrons, and Nuclei.**—The smallest particles which have so far been actually measured by means of the ultramicroscope are particles of colloidal gold which were  $1.7 \mu\mu$  in diameter ( $1 \mu\mu = 0.000001$  millimeter). Since from calculations based upon the kinetic molecular hypothesis it is estimated that a molecule of hydrogen has a diameter of  $0.1 \mu\mu$  and of starch  $5 \mu\mu$  it may be said that bodies the size of a molecule may yet be seen. Also based upon measurements of the number of  $\alpha$  particles given off by radium, which may be counted by means of the spinthariscopes (p. 581) and compared with the volume of helium produced, Rutherford has estimated that there are  $2.56 \times 10^{19}$  molecules of helium per cubic centimeter. Perrin has estimated the number by another method at  $3.15 \times 10^{19}$  and Millikan as  $2.7 \times 10^{19}$ . Jeans (Phil. Mag. 8, 692, 1904) gives the following table of the estimates of the diameter of molecules in  $\mu\mu$ :

H <sub>2</sub> .....	0.208	CO.....	0.286	air.....	0.284
He.....	0.187	C <sub>2</sub> H <sub>4</sub> .....	0.387	NO.....	0.282
H <sub>2</sub> O.....	0.339	N <sub>2</sub> .....	0.291	O <sub>2</sub> .....	0.273
A.....	0.279	N <sub>2</sub> O.....	0.352	Cl <sub>2</sub> .....	0.411
CO <sub>2</sub> .....	0.336				

These values are based on such a variety of methods which all give results of the same order of magnitude that we may be assured that the size of molecules and their relation to the space occupied is reasonably correct. The numbers are of course incomprehensibly small and Mellor attempts to give them significance by calling attention to the fact that it would take 40,000,000 molecules of air touching each other to make a row one inch in length, but that if all the molecules in a cubic inch of gas were laid in a row touching each other they would make a row 35,000,000 miles in length. In the monatomic molecules the atoms and molecules are of the same dimensions but with the diatomic and polyatomic molecules the

atoms are ordinarily considered to bear some such relation to each other as the planets of a solar system. The atoms must therefore be very much smaller than the molecules of which they are "component spheres." These atoms are now by the electron hypothesis considered as "made up of systems of concentric rings of electrons assembled within a sphere of positive electrification" (Thompson). Or, according to Rutherford, "each atom is supposed to be made up of a positively charged nucleus around which rotate the negative electrons." From the behavior of  $\alpha$  particles when striking gold foil the conclusion has been reached by Marsden that the positive nucleus of the gold atom has a maximum diameter of  $3.4 \times 10^{-13}$  cm. (or  $0.000034 \mu\mu$ ). Hydrogen atoms have a diameter of  $1.7 \times 10^{-13}$  cm., while the negative electron has a diameter of  $2 \times 10^{-13}$  cm. These are the maximum diameters. They may be less. If all these conclusions are accepted at their face value it is readily perceived that the actual **matter** of bodies is nearly negligible in quantity. Indeed, Lenard has indulged himself in a calculation by means of which he reaches the conclusion that the total matter of a cubic meter of platinum (density 21.4) is not greater than 1 cubic millimeter. If, however, we follow Kaufman and ascribe the mass of electrons to their motion, then indeed if the hydrogen nucleus is, as Rutherford suggests, the positive electron, we have resolved matter into energy wholly, and an atom and consequently all matter is, as Ostwald believes, energy solely. It is not to be understood from this somewhat cursory relegation of matter to the limbo of non-existence that anything very serious has been done. We are accustomed to expressing our knowledge of nature and its changes in terms of four fundamental concepts, space, time, matter, and energy. What has happened, therefore, is that this number of concepts is reduced to three and what we know as matter is but a particular form of energy manifestation. We have not disturbed the molecule as the fundamental unit of physical change nor the atom as the unit of chemical reaction. Ultimately this reduction to three concepts will doubtless result in increased simplicity of formulation of scientific knowledge. An example of this effect follows.

*Atomic Numbers.*—In 1913 Laue (Ann. Physik, 41, p. 989) discovered that when an element is used as an anticathode in an X-ray tube the X-rays produced were of a wave length characteristic of the element used. He and others developed a method of



obtaining the spectra of these radiations using crystal surfaces in lieu of the gratings used for ordinary light. Moseley (Phil. Mag. 26, 1024, 27, 703 (1913 and 1914)) studied these spectra photographically for all the elements between aluminium and gold. He found a remarkable relationship between the frequencies (wave lengths) of the *K* series of radiations. In going from one element to the one of next higher atomic weight the lines were shifted toward the violet end of the spectrum, *i.e.*, the wave lengths were lessened. Indeed, using the formula  $V = K(N - 1)^2$  where  $V$  = wave length,  $K$  = a constant, and  $N$  = a number arbitrarily chosen, there is a constant increase in the value of  $N$  for each successive element in the periodic table. If now the number  $N$  is chosen to correspond to the numerical order of the element in the periodic table for any element, *e.g.*, 13 for aluminium, successive values of  $V$  are 14 for silicon, 15 for phosphorus, etc. Moseley considers these numbers to be proportional to the nuclear charge upon the atoms (Van den Broek's Hypothesis, Phys. Zeit. 14, 33 (1913)), and proposes a periodic arrangement of the elements based upon these numbers, which are called **atomic numbers**. The most interesting point in this connection is that if these numbers are proportional to the nuclear charge it is possible to have two elements of the same atomic weight, provided the nuclear charge, *i.e.*, the atomic number, is different and to have **elements of different atomic weights with the same properties**, chemically at least, provided the nuclear charges are the same. This conception gives, then, a clue to the reason for the existence of isotopes such as have been found for lead (p. 584), for the radioactive elements (*cf.* p. 582), and another form of neon reported by Aston (Eng. 96, 423, 1913). It does not follow that the isotopes need have identical physical properties (*cf.* Harkins, Jour. Am. Chem. Soc., Vol. XXXVIII, p. 190).

**The Periodic Law.**—The outline of the development of the periodic law and the table, or tables, of Mendeleeff has been given in Chapter XI. That the situation is in many respects unsatisfactory was pointed out (p. 211). That such is the case is also evidenced by the fact that since 1870 at least sixty more or less different modes of expression of the fundamental principle of periodicity have been published (*cf.* Friend, Text-book of Inorganic Chemistry, Vol. 1, p. 276). That so many efforts have been made is also to be taken as evidence of the importance and

of the desirability of a more satisfactory system of classification. The introduction of the electron hypothesis of the structure of the atom and the Moseley atomic numbers, coupled with the evidence in favor of inorganic evolution, have led to a new crop of periodic systems which take the atomic numbers, and inferentially the nuclear charge, as the fundamental property. The most ambitious of these is that of W. D. Harkins of the University of Chicago (Jour. Am. Chem. Soc., Vol. 37, p. 169 (*q.v.*)). The table is in the form of a helix in space (Fig. 137), or as a spiral on a plane (Fig. 138). The advantages claimed for this means of expression of the law, which perhaps should now read **the properties of the elements are a periodic function of their atomic numbers**, are as follows: (1) The relation between main and sub-groups are graphically and correctly shown; (2) the table arranges the elements in the exact order of atomic numbers and gives no blanks where corresponding blanks do not occur in the atomic numbers as shown by the X-ray spectra of the elements; (3) it plots the atomic weights so that isotopes may be shown; (4) both the 0 and 8th groups fit naturally into the system; (5) the valence, the general chemical properties, the density, the melting points, etc., are all appropriately related to the table. It will be observed that if this table correctly represents the situation there are yet to be discovered, in this system, five elements, three in group seven, ekamanganese I (at. wt. 99), ekamanganese II (at. wt. 188), ekaiodine (at. wt. 219), one in group I, ekacaesium (at. wt. about 225), one rare earth called ekaneodymium (at. wt. 146). These, with the known elements, make a total of 92. In addition to these we may have, as claimed by Nicholson, from a study of the spectra of the stars, a group of elements outside this system. These are called by Nicholson (Phil. Mag. 22, 541, 28, 90), protohydrogen, nebulium, protofluorine (or coronium), and arconium. Their existence is problematical. There may also be elements of greater atomic weight than uranium, but no indications of such are at hand and the instability of the last cycle prompts the suggestion that they do not occur.

**The Theories of Valency.**—What may be considered the fact of valency is that the atomic weights of the elements have different combining capacities. When measured in terms of hydrogen we have seen that the elements show a valence range



## INORGANIC CHEMISTRY

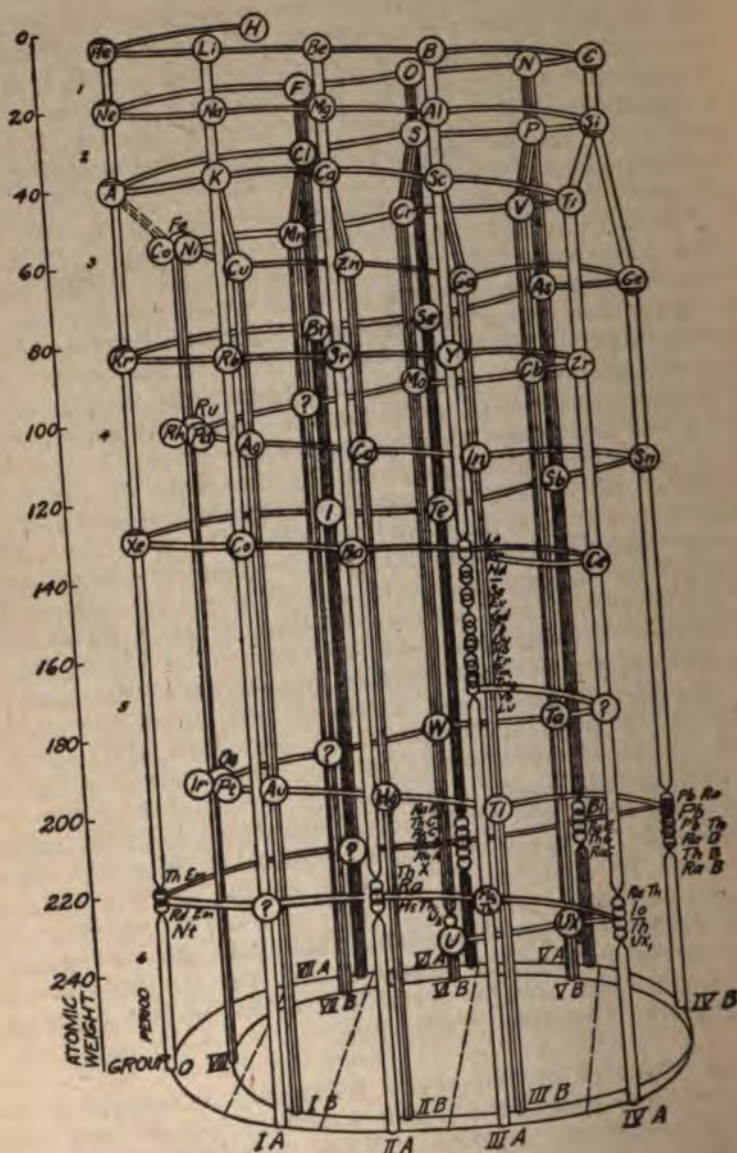


FIG. 137.





of from one to eight. There have been many attempts to explain this relation. Reference has been made to some of these in previous pages (*cf.* p. 615 and p. 617). The view of Abegg, which was developed from chemical considerations, is that every element possesses a valence of eight and that this total is made of both negative and positive factors. (This suggestion was first made by Mendeleeff.) The valence type ordinarily manifested by an element is called its **normal** valence while the remaining valence is called its **contra-valence**. The normal valence is the stronger and is positive for metals, and negative for non-metals. Only in the case of the eighth group is the maximum valence ever operative in a single compound. This assumption accounts for positive valence of chlorine, etc., in their oxygen compounds and for the behavior of chlorine in nitrogen chloride (*cf.* p. 270), and many very interesting reactions. It does not, however, offer any explanation of why these valencies exist. With the development of the electron hypothesis there has come an explanation which is perhaps already to be considered the orthodox theory of valency. The fundamental suggestion was first made by J. J. Thompson in 1903. When atoms are regarded as complexes of negative electrons surrounding a nuclear positive charge the number of electrons must be constant as long as the atom remains neutral. If, however, one or more negative electrons leave an atom it becomes positively charged and is thus capable of attracting negatively charged bodies. Electronegative elements are those the atoms of which may assume negative electrons, while electropositive elements are those capable of losing negative electrons. Chemical combinations are a result of the attraction between these "ionized" atoms. There is a veritable flood of hypotheses concerning the relation of the electrons when the elements are free and also with respect to their relation to the atoms of compounds. A summary of some of these is found in Mellor's *Modern Inorganic Chemistry* (p. 864 *et seq.*). It may be remarked that there is a very marked disproportion between conjecture and experimental data. At present the chief apparent value of the electronic conception of valence lies in the simple relation it expresses between oxidation and reduction. There is the possibility that it may also furnish a simpler mode of classification of chemical facts (see Nelson and Falk, *Jour. Am. Chem. Soc.*, Vol. 37, p. 274). The value of the suggestions of Nelson have not yet been demonstrated.

**Conclusion.**—The survey of the field of chemistry which is the purpose of the preceding pages is now finished. That it is not really complete the writer knows full well. If, however, the reader who has had the courage and persistence to follow through to this point shall feel that he has had a glimpse of a field of human knowledge which leaves him with a desire for a more intimate acquaintance the time spent will have been far from wasted. If in addition to this the method of presentation shall have developed or increased the habit and facility in the use of the scientific method an additional benefit will have been gained. If, further, the reader has a clearer grasp of the great principles of science as illustrated by chemical facts, a clearer conception of the relation of fact to hypothesis, a better conception of the use of imagination in science, a more comprehensive view of the interrelatedness of nature and an increased admiration for its beauty he will be indeed profited. All these the writer hopes may have accrued to the reader. The facts of chemistry presented are of necessity only a small fragment of the whole. It is hoped and believed that they are as accurate as our present state of knowledge permits. The hypotheses have been stated in outline as clearly as possible and so far as possible without dogmatic assertion. The student is urged to obey the injunction of the Great Apostle and "prove all things; hold fast that which is good," and also, to "stand fast and hold the traditions which ye have been taught," knowing that by the use of hypotheses we build the structure of science and that they are not the chief object of its consideration.

The primal purpose of scientific study is to obtain increased control over, or knowledge of, nature's processes, so that we may be better able to solve the problems of life whether of material or spiritual character. The thing, then, of fundamental importance is **Truth**. "Exalt her and she shall promote thee."



## APPENDIX

### I. Metric System

Length: 1 centimeter (cm.) = 0.3937 in.; 100 cm. = 1 meter (m.).

Volume: 1 liter (l.) = 1.057 U. S. quarts; 1000 cubic centimeters (cc.) = 1 l.

Weight: 1 kilogram (kilo.) = 2.205 lbs., avoird., 1000 grams (g.) = 1 kilo.

### II. Vapor Pressure of Water in Millimeters of Mercury

Temperature°	-3	0	4	6	8	10	11	12	13	14	15
Pressure.....	3.7	4.6	6.1	7.0	8.0	9.1	9.8	10.5	11.1	11.9	12.7
Temperature°	16	17	18	19	20	21	22	23	24	25	26
Pressure.....	13.6	14.5	15.5	16.5	17.5	18.8	19.7	21.0	22.2	23.5	25.0
Temperature°	27	28	29	30	35	40	45	50	60	70	80
Pressure.....	26.5	28.1	29.7	31.5	41.9	55.3	71.4	91.98	148.9	233.3	354.9
Temperature°	90	100	125	150	200	.....	.....	.....	.....	.....	.....
Pressure.....	526.5	760	1744	3581	11,689	.....	.....	.....	.....	.....	.....

### III. Temperature Corrections for the Barometer Reading at the Temperature Indicated to the Corresponding Height at 0°

Temperature°.....	.....	.....	4	10	11	12	13	14	15	16
Correction.....	.....	.....	0.5	1.3	1.4	1.6	1.7	1.8	2.0	2.1
Temperature°.....	.....	17	18	19	20	21	22	23	24	25
Correction.....	.....	2.2	2.4	2.5	2.6	2.8	2.9	3.0	3.1	3.3
Temperature°.....	26	27	28	29	30	31	32	33	34	35
Correction.....	3.4	3.5	3.7	3.8	3.9	4.0	4.1	4.3	4.4	4.5

## IV. Specific Gravity and Melting Point of the Elements

Element.	Specific gravity.	Melting point, deg. C.	Element.	Specific gravity.	Melting point, deg. C.
Antimony.....	2.60	654.5	Magnesium.....	1.74	632.6
Barium.....	6.62	425-450	Manganese.....	7.39	1900
Bismuth.....	5.73	.....	Mercury.....	13.55	-38.85
Calcium.....	3.75	85	Molybdenum.....	8.6	w. h.
Carbon.....	9.8	268.3	Nickel.....	8.9	1450
Cerium.....	2.5	(?)	Osmium.....	22.48	2500
Cobalt.....	3.15	-7.3	Palladium.....	11.4	1500
Copper.....	8.64	316	Phosphorus.....	1.83	44.2
Fluorine.....	1.88	26.5	Platinum.....	21.5	1779
Gallium.....	1.58	760	Potassium.....	0.87	58
Germanium.....	.....	.....	Rhodium.....	12.1	2000
Hydrogen.....	3.52	.....	Rubidium.....	1.52	38.5
Iodine.....	2.3	.....	Ruthenium.....	12.26	1800 (?)
Iron.....	1.8	.....	Selenium.....	4.80	217
Lead.....	6.68	623	Silicon.....	2.39	(?)
Lithium.....	6.50	1515	Silver.....	10.50	954
Magnesium.....	8.6	1800	Sodium.....	0.98	95.6
Manganese.....	8.93	1054	Strontium.....	2.54	(?)
Mercury.....	5.95	30.15	Sulphur:	.....	.....
Molybdenum.....	5.47	900	(a) Rhombic.....	2.07	114.5
Nickel.....	1.93	900 (?)	(b) Monoclinic.....	1.96	120
Osmium.....	19.32	1035	Tellurium.....	6.25	452
Palladium.....	7.42	176	Thallium.....	11.85	290
Phosphorus.....	4.95	113-5	Titanium.....	3.54	(?)
Potassium.....	22.42	2200	Tin.....	7.29	232.7
Rhodium.....	7.86	1587	Tungsten.....	19.1	2900 (?)
Rubidium.....	6.1	(?)	Uranium.....	18.7	w. h.
Selenium.....	11.37	322	Vanadium.....	5.5	(?)
Silver.....	0.59	180	Zinc.....	7.1	415.3



## V. Energy, Power, and Pressure Units

10,000,000 ergs	= 1 joule.
1 cal.	= 4.187 joules.
1 B.t.u.	= 1055 joules = 252 cal.
1 foot pound	= 1.356 joules = 0.3240 cal.
1 horse power	= 33,000 foot pounds per minute.
1 horse power	= 746 watts.
1 watt	= 10,000,000 ergs = 1 joule per second.
1 atmosphere	= 760 mm. of mercury per sq. cm.
1 atmosphere	= 1033 g. per sq. cm. = 14.696 lbs. per sq. in.

## VI. Percentage Composition of Certain Alloys

It is to be noted that alloys vary considerably in composition. The values given are but approximate.

Brass.....	Cu, 63-72; Zn, 27-34.
Brass.....	Cu, 66-70; Pb, 0.3-0.5; Zn, 33.7-29.5.
Bronze (for bearings).....	Cu, 82; Sn, 16; Zn, 2.
Bronze (art bronze).....	Cu, 82.7; Sn, 4.7; Pb, 9.8; Zn, 1.8.
Gun metal.....	Cu, 91; Sn, 9.
Babbitt.....	Cu, 1.5; Sn, 45.5; Pb, 40; Sb, 13.
Babbitt.....	Cu, 1; Sn, 19; Pb, 5; Zn, 69; Sb, 3.
Soft solder.....	Sn, 50; Pb, 50.
Plumber's solder.....	Sn, 33.3; Pb, 66.7.
Rose's metal.....	Sn, 22.9; Pb, 27.1; Bi, 50.
Car-box metal.....	Pb, 84.3; Zn, 0.7; Sb, 14.4; Fe, 0.6.
Type metal.....	Sn, 3; Pb, 82; Sb, 15.
Stereotype metal.....	Cu, 2; Sn, 10; Pb, 70; Sb, 18.
White metal (very variable).....	Cu, 2.4; Sn, 53; Pb, 33; Zn, 1; Sb, 10.6.
Wood's metal.....	Sn, 14; Pb, 24; Bi, 50; Cd, 12.
German silver.....	Cu, 57; Zn, 19; Ni, 24.
Nickel coin, U. S.....	Cu, 75; Ni, 25.
Silver coin, U. S.....	Ag, 90; Cu, 10.
Gold coin, U. S.....	Au, 90; Cu, 10.
Magnalium.....	Al, 90; Mg, 10.
Tungsten steel.....	C, 2-1.3; Si, 0.15-0.5; Mn, 0.5-2; Mo 0-1.0; W, 1-3; V, 2; Fe, 92-97.

**III. Conductivity of Metals in Mho's (Reciprocal Ohms) per Centimeter Cube at 0°**

Aluminium.....	$38.2 \times 10^4$	Manganese.....	$18.2-22.7 \times 10^4$
Antimony.....	$2.6 \times 10^4$	Magnesium.....	$23.2 \times 10^4$
Arsenic.....	$2.0 \times 10^4$	Sodium.....	$22.3 \times 10^4$
Lead.....	$5.1 \times 10^4$	Nickel.....	$14.4 \times 10^4$
Cadmium.....	$14.4 \times 10^4$	Osmium (20°).....	$10.5 \times 10^4$
Caesium.....	$5.18 \times 10^4$	Palladium.....	$9.79 \times 10^4$
Calcium (20°).....	$9.5 \times 10^4$	Platinum.....	$8.94 \times 10^4$
Chromium.....	$38.5 \times 10^4$	Mercury.....	$1.063 \times 10^4$
Iron.....	$9.36 \times 10^4$	Rhodium.....	$21.3 \times 10^4$
Pig iron.....	$1.02 \times 10^4$	Rubidium.....	$8.6 \times 10^4$
Gallium.....	$1.87 \times 10^4$	Silver.....	$67.2 \times 10^4$
Gold.....	$44.5 \times 10^4$	Silicon.....	$1.7 \times 10^4$
Indium.....	$11.95 \times 10^4$	Strontium (20°).....	$4.03 \times 10^4$
Iridium.....	$14.3 \times 10^4$	Thallium.....	$5.56 \times 10^4$
Cobalt (20°).....	$10.3 \times 10^4$	Bismuth.....	$0.92 \times 10^4$
Copper.....	$63.4 \times 10^4$	Tin.....	$8.7 \times 10^4$
Lithium.....	$11.7 \times 10^4$	Zinc.....	$17 \times 10^4$



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## ERRATA SHEET

### INORGANIC CHEMISTRY — BYERS

- Page 14 Line 17, for: "nitrous oxide" read: "nitric oxide"  
 Line 18, for: "nitric oxide" read: "nitrogen peroxide"
- Page 20 Line 18, for: "of one of" read: "of one"
- Page 81 Line 3, for: " $\text{H}_2\text{O}$ " read: " $3\text{H}_2\text{O}$ "
- Page 125 Heading: for: "Hydrogen Chlorine" read: "Hydrogen Chloride"
- Page 154 Line 7, for: " $\text{Zn} + 2\text{HBr} \rightarrow \text{ZnBr}_2 + \text{H}_2\text{O}$ "  
 read: " $\text{Zn}(\text{OH})_2 + 2\text{HBr} \rightarrow \text{ZnBr}_2 + 2\text{H}_2\text{O}$ "
- Page 177 Line 17 from bottom, for: " $18^\circ$  is" read: " $16^\circ$  and is"
- Page 209 Line 12, for: "Series 2" read: "Series 11"
- Page 224 Line 17, for: " $5\text{H}_2\text{S} \rightarrow 3\text{H}_2\text{O}$ " read: " $5\text{H}_2\text{S} \rightarrow 6\text{H}_2\text{O}$ "  
 Line 28, for: "S" read: "2S"
- Page 236 Line 9 from bottom, for: "sulfate" read: "sulfur"
- Page 242 Line 6 from bottom, for: " $\text{Na}_2\text{S}_2\text{O}_8$ " read: " $\text{Na}_2\text{S}_2\text{O}_5$ "
- Page 254 Line 3 from bottom, for: "Fig. 68" read: "Fig. 69"
- Page 265 Line 1 from bottom, for: "15.7" read: "14.7"
- Page 277 In Table under Helium, for: "3.39" read: "3.99"
- Page 279 Line 5 from bottom, for: "when" read: "at which"
- Page 289 Middle of page, for: " $\text{C}_{12}\text{H}_{14}(\text{NO}_2)_6$ " read: " $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{NO}_2)_6$ "
- Page 303 Line 18, for: " $\text{P}_2\text{O}_5 \rightarrow \text{P}_2\text{O}_5 + \text{O}_2$ " read: " $2\text{P}_2\text{O}_5 \rightarrow 3\text{P}_2\text{O}_5 + 2\text{P}$ "
- Page 304 Table, for:  $\begin{array}{c} \text{O} \\ // \\ \text{P} = \text{O} \\ // \\ \text{O} \\ // \\ \text{O} \\ // \\ \text{O} \\ // \\ \text{P} = \text{O} \\ // \\ \text{O} \end{array}$  read:  $\begin{array}{c} \text{O} \\ // \\ \text{P} = \text{O} \\ // \\ \text{O} \\ // \\ \text{O} \\ // \\ \text{O} \\ // \\ \text{P} = \text{O} \\ // \\ \text{O} \end{array}$
- Also, for: last " $\text{H}_2\text{O}$ " read: " $2\text{H}_2\text{O}$ "
- Page 312 Line 8 from bottom, for: " $\text{H}_2\text{O}$ " read: " $3\text{H}_2\text{O}$ "
- Page 362 Line 22, for: " $(\text{C}_{12}\text{H}_{14}\text{O}_4)_6$ " read: " $\text{C}_{12}\text{H}_{14}\text{O}_4$ "  
 Line 23, for: " $(\text{C}_{12}\text{H}_{14}\text{O}_4)_6$ " read: " $\text{C}_{12}\text{H}_{14}\text{O}_4$ "  
 Line 26, for: " $\text{C}_2\text{H}_5(\text{C}_{12}\text{H}_{14}\text{O}_4)_6$ " read: " $\text{C}_2\text{H}_5(\text{C}_{12}\text{H}_{14}\text{O}_4)_6$ "
- Page 489 Line 13, for: "it" read: "is"
- Page 502 Line 1 from bottom, for: "Fig. 4" read: "Fig. 111"
- Page 590 Line 9 from bottom, for: " $\text{MnO}_2$ " read: " $2\text{MnO}_2$ "
- Page 605 Line 1 from bottom, for: " $2\text{Fe}_2\text{O}_3$ " read: " $2\text{Fe}_2\text{O}_1$ "











# VII. Table of Atomic Weights

ne of element.	Symbol.	Atomic weight, 1914.	Elementary substance first isolated by	Date.
n. (Stibium).....	Al	27.1	Wohler.....	1827
.....	Sb	120.2	Basil Valentine.....	15th cent
.....	A	39.9	Rayleigh and Ramsay.....	1894
.....	As	74.96	Albertus Magnus.....	13th cent
.....	Ba	137.37	Davy.....	1808
.....	Bi	208.0	Ment. by Basil Valentine.....	15th cent
.....	B	11.0	Gay-Lussac and Thenard.....	1808
.....	Br	79.92	Balard.....	1826
.....	Cd	112.4	Stromeyer.....	1817
.....	Cs	132.81	Bunsen and Kirchhoff.....	1861
.....	Ca	40.07	Davy.....	1808
.....	C	12.005	Prehistori.....	
.....	Ce	140.25	Mosander.....	1839
.....	Cl	35.46	Scheele.....	1774
.....	Cr	52.0	Vauquelin.....	1797
.....	Co	58.97	Brand.....	1735
m (Niobium).....	Cb	93.5	Hatchett.....	1801
prum).....	Cu	63.57	Prehistori.....	
m.....	Dy	162.5	Boisbaudran.....	1886
.....	E	167.7	Mosander.....	1843
.....	Eu	152.0	Demarcay.....	1901
.....	F	19.0	Moissan.....	1886
n.....	Gd	157.3	Marignac and Boisbaudran.....	1886
.....	Ga	69.9	Lecoq de Boisbaudran.....	1875
m.....	Ge	72.5	Winkler.....	1886
(Beryllium).....	Gl	9.1	Wohler and Bussy.....	1828
um).....	Au	197.2	Prehistori.....	
.....	He	3.99	Ramsay and Cleve.....	1898
.....	Ho	163.5	Soret.....	1879
.....	H	1.008	Cavendish.....	1766
.....	In	114.8	Reich and Richter.....	1863
.....	I	126.92	Courtois.....	1811
.....	Ir	193.1	Smithson Tennant.....	1804
um).....	Fe	55.84	Prehistori.....	
.....	Kr	82.92	Ramsay and Travers.....	1898
n.....	La	139.0	Mosander.....	1839
nbum).....	Pb	207.2	Mentioned by Pliny.....	Prehistori
.....	Li	6.94	Arfvedson.....	1817
.....	Lu	175.0	Welsbach.....	1906
.....	Mg	24.32	Liebig and Bussy.....	1830
.....	Mn	54.93	Gahn.....	1774
Hydrargyrum).....	Hg	200.6	First ment. by Theophrastus.....	300 a.c.
um.....	Mo	96.0	Hjelm.....	1790
.....	Nd	144.3	Auer von Welsbach.....	1885
.....	Ne	20.2	Ramsay and Travers.....	1898
.....	Ni	58.68	Cronstedt.....	1751
.....	Nt	222.4	Rutherford.....	1903
.....	N	14.01	Rutherford.....	1772
.....	Os	190.9	Smithson Tennant.....	1804
.....	O	16.0	Priestley.....	1774
.....	Pd	106.7	Wollaston.....	1803
.....	P	31.04	Brand.....	1674
.....	Pt	195.2	Watson.....	1748
(Kalium).....	K	39.10	Davy.....	1807
ium.....	Pr	140.9	Auer von Welsbach.....	1885
.....	Ra	226.0	Curie.....	1903
.....	Rh	102.9	Wollaston.....	1803
.....	Rb	85.45	Bunsen and Kirchhoff.....	1861
.....	Ru	101.7	Claus.....	1845
.....	Sa	150.4	Lecoq de Boisbaudran.....	1879
.....	Sc	44.1	Nilson and Cleve.....	1879
.....	Se	79.2	Berzelius.....	1817
.....	Si	28.3	Berzelius.....	1823
entum).....	Ag	107.88	Prehistori.....	
atrium).....	Na	23.00	Davy.....	1807
.....	Sr	87.63	Davy.....	1808
.....	S	32.06	Prehistori.....	
.....	Ta	181.5	Ekeberg.....	1802
.....	Tb	159.2	Mosander.....	1843
.....	Te	127.5	Muller von Reichenstein.....	1782
.....	Tl	204.0	Crookes.....	1861
.....	Th	232.4	Berzelius.....	1828
.....	Tm	168.5	Cleve.....	1880
um).....	Sn	118.7	Prehistori.....	
.....	Ti	48.1	Gregor.....	1789
Wolfram).....	W	184.0	Scheele.....	1781
.....	U	238.2	Peluz.....	1841
.....	V	51.0	Berzelius.....	1817
.....	X	130.2	Ram.....	18
.....	Yb	173.5	Marignac.....	18
.....	Yt	88.7	Gad.....	14
.....	Zn	65.37	Mend.....	1869
.....	Zr	90.6	Berzelius.....	25



